

SAND REPORT

SAND 2001-2266

Unlimited Release

Printed September, 2001

Interactions of UPO IONSIV IE-911® with Pretreatment and Simulant Solutions (UOP batches 98-5, 99-7, 99-9)

May D. Nyman
Thomas J. Headley
Tina M. Nenoff

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation,
a Lockheed Martin Company, for the United States Department of
Energy under Contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.



Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States
Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865)576-8401
Facsimile: (865)576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: <http://www.doe.gov/bridge>

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd
Springfield, VA 22161

Telephone: (800)553-6847
Facsimile: (703)605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: <http://www.ntis.gov/ordering.htm>



SAND 2001-2266
Unlimited Release
Printed September 2001

**Interactions of UOP IONSIV IE-911[®] with Pretreatment and
Simulant Solutions (UOP batches 98-5, 99-7, 99-9)**

May Nyman and Tina M. Nenoff
Environmental Monitoring and Characterization Department

Thomas J. Headley
Materials Characterization Department

Sandia National Laboratories
P O Box 5800
Albuquerque, NM 87185-0755

Abstract

Ion exchange columns of UOP IONSIV[®] IE-911 (zirconia bound crystalline silicotitanate (CST) ion exchangers) is one technology currently under consideration by the Department of Energy for removal of ¹³⁷Cs from the radioactive wastes stored at the Savannah River Site. Recent CST batch and column tests at Savannah River Site (SRS) and Oak Ridge National Laboratory (ORNL) have suggested that CST performance is degraded and have demonstrated column plugging, which have raised some concerns about the operability regime of these materials. These incidents include: 1) IE-911 pretreated with NaOH formed Nb-rich solids that plugged the top layer (i.e. entrance region) of a column. Analyses of the pre-wash solutions also show high concentrations of Nb. 2) IE-911 exposed to alumina-containing simulant (i.e. average salt simulant) nucleated the growth of sodium aluminosilicate phases such as cancrinite on the surface

of the bound pellets, and thus cemented pellets together and filled interstitial spaces. 3) High temperature exposure (50-120 °C) of IE-911 results in loss of Cs capacity and almost complete degradation of CST at 120 °C.

To understand the cause and mechanism of these phenomena and thus avoid future performance degradation issues, a comprehensive series of pre-treatment, simulant treatment, and column and batch studies are under investigation as a multi-lab effort. The treatment experiments are being performed at SRS, ORNL and Pacific Northwest National Laboratory (PNNL); and samples are analyzed at Sandia National Laboratories (SNL).

Characterization studies at SNL thus far have revealed:

- In addition to binder and CST, the as-received IE-911 contains three impurity phases including a niobium titanate. This phase may be the source of the Nb oxide-rich column plug that forms during pre-treatment with recirculating NaOH.
- NaOH pretreatment and simulant treatment of IE-911 results in a cracking/exfoliation degradation, which may be related to the formation of fines. Increased temperature or time of exposure of IE-911 to simulant (both aluminum-containing and aluminum-free) results in accelerated morphology (cracking/exfoliation) changes.
- The cracking /exfoliation degradation does not appear to affect Cs K_d values.
- IE-911 treated with alumina-containing simulant results in cancrinite formation on pellet surfaces.
- Cancrinite formation increases with increasing temperature and time of simulant exposure. Cancrinite deposition is correlated with Cs K_d drop.
- Exposure of IE-911 to simulant at 23 – 80 °C does not significantly change the composition of the pellets. Exposure at 120 °C to simulant results in almost complete decomposition of the CST.

Future work on this ongoing project includes;

- Characterization of the short-term exposure samples recently received from PNNL.
- Compile, compare and contrast the characterization data of simulant-treated samples from SRS, ORNL and PNNL.
- Determine the cause and mechanism of the cracking/exfoliation and evaluate its effect on material performance.
- Confirm identity of the niobium titanate impurity as a source of Nb oxide for plug formation and devise a recommendation for IE-911 treatment to avoid this plug formation (in conjunction with J. Krumhansl, SNL).

CONTENTS

1.0 Introduction	6
2.0 Experimental.....	8
2.1 Sample Log	8
2.2 Instrumentation.....	8
3.0 Results and Discussion	10
3.1 Choice of Instrumentation	10
3.2 Characterization of H-IE-911 (as received) and Na-IE-911 (pretreated)	10
3.3 Batch Simulant Studies	15
3.4 Column Studies (ORNL).....	22
4.0 Summary and Conclusions.....	26
5.0 Cited References	27
6.0 Acknowledgements	28
Appendix A. Sample Log of Simulant-treated IE-911 from ORNL and SRS.	29
Appendix B. Additional XRPD Spectra of IE-911 Samples from ORNL and SRS.	32
Appendix C. Addendum on Exfoliation and Cracking Phenomenon.....	39

1.0 INTRODUCTION

The radioactive inventory in Savannah River Site waste tanks is comprised mainly of ^{137}Cs and ^{90}Sr . A down-select of a technology for ^{137}Cs removal from the salt waste is currently underway. The Department of Energy plans to have this decision finalized within a year. Ion exchange utilizing columns of Crystalline Silicotitanate (CST) is one technology under consideration. The CST ion exchanger is an inorganic material with superior properties for this application including: 1) excellent Cs selectivity in presence of high concentrations of competing ions (i.e. Na), 2) stability in extreme chemical environments (acidic or caustic solutions) and 3) stability in extreme radiation fields. Recent column and batch testing of the bound form of CST (UOP IONSIV[®] IE-911 manufactured by UOP LLC, Des Plaines, Illinois) carried out at ORNL and SRS have given test results which have raised some issues concerning the performance of these engineered materials under certain operating conditions.

The material performance issues of concern are all related to batch testing and column plugging incidents observed at ORNL and SRS over the past two years, which are summarized in an interoffice memorandum by D. D. Walker in August 2000.¹ The three following activities produced results of concern: 1) IE-911 pretreated with NaOH formed Nb-rich solids that plugged the top layer of a column.² Analyses of the pre-wash solutions also show high concentrations of Nb. 2) IE-911 exposed to alumina-containing simulant (i.e. average salt simulant) nucleated the growth of sodium aluminosilicate phases³ such as cancrinite on the surface of the bound pellets, and thus resulted in partial cementation and interstitial space filling. 3) Batch testing at ORNL show that heating Cs-loaded CSTs (>50 °C) may result in irreversible Cs desorption from the CSTs.⁴ Furthermore, thermal instability (>50 °C) of CST was first noted in 1996 at Sandia National Laboratories in a report by Nenoff et al.⁵ These results are interrelated in the actual implementation of radioactive waste separations, in that column plugging results in stoppage of flow, and consequently, radiogenic heating of the columns and their contained materials.

The material performance issue of Nb-oxide column plug formation is directly related to the UOP binding process, which requires the conversion of the CSTs from the as-synthesized sodium form (Na-CST) to the acid form (H-CST). As a result, the bound ion exchanger is not in equilibrium with the highly caustic simulant solutions (pH>13). Therefore, a NaOH-pretreatment step is required to avoid precipitation of aluminum hydroxide from the simulant solution as the pH drops upon exposure to IE-911. It is this combination of acid followed by base treatment of IE-911, which results in leaching of a niobate-based impurity phase which subsequently may contribute to column plugging. The issue of CST degradation at high temperatures is also related to the material composition. Although the CSTs are extremely robust zeotype materials, they are by nature open-framework materials that are notoriously unstable at high temperatures. On the other hand, the material performance issue of aluminosilicate formation is inherent to the nature of the extremely basic, alumina-containing simulants. In any case, these issues must be addressed to ensure optimum performance of the IE-911 ion exchangers.

The performance issues of current concern are summarized as:

- Plugging caused by Nb oxide dissolution and re-precipitation during pretreatment of IE-911 with recirculating NaOH (column conditioning)
- Plugging caused by aluminosilicate precipitation during exposure of IE-911 to alumina-containing simulant solutions
- Possible drop in Cs K_{α} resulting from pore blockage by the precipitated aluminosilicate phases
- Desorption of Cs from IE-911 heated in simulant ($> 50^{\circ}\text{C}$)

The objective of the work described in this report is to provide systematic and consistent characterization data of as-received, pre-treated and simulant-treated IE-911 samples [pre-treatment and simulant-treatment performed at ORNL, SRS and PNNL] to contribute to the understanding and thus prevention of column plugging. Characterization studies are designed to reveal:

- The source (i.e. an impurity phase) of the Nb-oxide dissolved during the NaOH-pretreatment
- The conditions under which Na aluminosilicate precipitation occurs, and the mechanism of this process
- The cause of Cs K_{α} drop and Cs desorption in IE-911 heated ($>50^{\circ}\text{C}$) during simulant exposure

The major tools used for this characterization study include 1) X-ray powder diffraction (XRPD), 2) Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM/EDS), 3) Transmission Electron Microscopy/Energy Dispersive Spectroscopy (TEM/EDS) 4) Direct Coupled Plasma Spectroscopy (DCP), and 5) Infrared Spectroscopy (IR).

Continued work in the latter parts of these studies (in conjunction with column studies led by J. L. Krumhansl at Sandia National Laboratories and short term stability studies led by M. L. Balmer at Pacific Northwest National Laboratory) will provide:

- Suggestions for pre-treatment regimes to rid the IE-911 of the column-plugging Nb-source
- Guidelines for a temperature-time operating scheme in which the IE-911 remains highly functional (i.e. Cs K_{α} drop, and Na aluminosilicate deposition minimized)

2.0 EXPERIMENTAL

2.1 Sample Log

As-received IE-911. Samples of the acid-form (H-IE-911) of IE-911 provided for analysis include UOP Lots 9990-99-810007 and 89-99020-81000009 (99-7 and 99-9, respectively). The 99-7 batch was sent by P. Taylor at ORNL. We received two batches of 99-9; one from D. D. Walker and one directly from UOP LLC.

NaOH-pretreated IE-911. Samples of the Na-form (Na-IE-911) were prepared from UOP Lots 99-7 and 9990-98-810005 (98-5) at ORNL and UOP Lot 99-9 at SRS using a standardized procedure.⁶

Simulant Batch Studies

Description of Simulants. The simulant solutions used in these studies include; 1) average salt solution, 2) high pH salt solution, 3) high-nitrate salt solution and 4) high-hydroxide salt solution, which are described in detail in Walker's pretreatment guidelines.⁶ The important details to note for this study are summarized here. The average salt solution, high-nitrate salt solution and high hydroxide salt solution all contain ~0.3 molar $\text{Al}(\text{OH})_4^-$. The difference between these three solutions is: 1) The average salt solution contains approximately 2 moles sodium nitrate and 2 moles sodium hydroxide. 2) The high-nitrate salt solution contains approximately 3 moles sodium nitrate and 1 mole sodium hydroxide. 3) The high-hydroxide salt solution contains approximately 1 moles sodium nitrate and 3 moles sodium hydroxide. The high pH salt solution contains no AlO_2^- .

ORNL temperature studies. Samples of NaOH-pretreated UOP Lot 98-5 were exposed to average salt simulant for 86 days each at 23, 50, 80 and 120 °C. The IE-911 samples were then filtered and rinsed, and air-dried and sent to SNL in July 2000. Cs K_d values were reported with this suite of samples.⁴

SRS simulant composition studies. IE-911 was exposed to average-salt simulant, high-nitrate simulant, high-hydroxide simulant, deionized H_2O , and average-salt simulant with added H_2O_2 , CO_3^{2-} , and $\text{C}_2\text{O}_4^{2-}$ for 2 months each at room temperature. These IE-911 samples were sent to SNL in August 2000, where they were filtered, rinsed and air-dried. Cs K_d values were not reported with this suite of samples.⁷

Simulant-time Column Studies.

Samples of Na-IE-911 batch 98-5 were treated with average-salt simulant and high-pH salt simulant at room temperature in recirculating columns. Samples were removed from the center of the column at 1, 2, 3, 4, 4.5 and 5 months. Samples were rinsed, air-dried and sent to SNL in July 2000. Cs K_d values were reported with this suite of samples.⁴

2.2 Instrumentation

X-ray Powder Diffraction (XRPD). Samples for XRPD were ground using a mortar and pestle and mounted as a loose powder in a well-type Probering sample holder. The diffraction data were obtained from a Bruker AXS D8 Advance instrument with a $\text{Cu-K}\alpha$

source and solid-state (Kevex) detector. Data were collected in the range of $2\theta = 5-60^\circ$ with a step size of 0.05° and a step time of 5 seconds. Samples were rotated (~ 30 rpm) during data collection to eliminate the effects of specimen inhomogeneities.

Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS).

IE-911 pellets for SEM/EDS analyses were mounted whole (i.e. not crushed) onto a carbon disc using epoxy, and carbon-coated to eliminate sample charging. Images and EDS data were collected on a JEOL JSM-T300 SEM with energy dispersive capabilities.

Transmission Electron Microscopy/Energy Dispersive Spectroscopy (TEM/EDS)

Samples are prepared for TEM analysis by grinding a small quantity of the pellets in butanol and dispersing the slurry to dry on lacey carbon substrates on Cu support grids. TEM imaging, electron diffraction, and elemental analysis of phases in the samples are performed on a Philips CM30 TEM at 300 kV, equipped with an Oxford Instruments EDS spectrometer with a low-Z window to facilitate light element analysis.

Direct Coupled Plasma Spectroscopy (DCP)

DCP analyses were obtained from a FISONs instrument SS-7 DCP equipped with a plasma argon-air flame. Powder samples of IE-911 for wet chemical analysis were digested in 40% HF and diluted with DI water. For the elements Si, Ti, Nb and Zr, 5 and 20 ppm aqueous standards were prepared by appropriate dilutions of the 1000 ppm SPEX Plasma standards. Similarly, 2 and 6 ppm standards were prepared for Na. To eliminate matrix effects for the Nb analyses, it was necessary to add Na, Si, Ti, and Zr to the Nb standards in relative concentrations equivalent to those which are found in the IE-911 samples. To account for drift correction, standards were run before and after analyses, and sample concentrations were corrected using a time-concentration curve.

Infrared (IR) Spectroscopy.

Samples for IR Spectroscopy were ground with CsI (1-3 wt % IE-911 in CsI matrix) and pressed into a pellet. Data were collected on a Perkin-Elmer Spectrum GX FTIR System in the mid-IR range ($370-7800\text{ cm}^{-1}$), 20 scans.

^{29}Si solid state Nuclear Magnetic Resonance (NMR) Spectroscopy.

NMR spectra were obtained on a Bruker AMX400 at 79.5 MHz for ^{29}Si . Spectra were obtained using direct single pulse excitation, with 240 second recycle delay with 64 scans.

3.0 Results and Discussion

3.1 Choice of Instrumentation.

The variety of tools utilized in this characterization study provided numerous complementary data to approach an understanding of the IE-911 characteristics in their as-received (H-IE-911), pre-treated (Na-IE-911) and post-simulant treated forms. XRPD gave information on the structure, quality and relative concentrations of crystalline phases present in (> 5% abundance) in the material. This is predominantly the CSTs and any crystalline alteration products, inasmuch as the zirconia-based binder is amorphous. The SEM/EDS proved useful for imaging morphology on the micron length scale, such as the intact, engineered pellets (300-500 μm diameter). The EDS capability allows for identification of elements, as well as rough quantification so that compositional trends may be observed. The TEM/EDS provided similar information as the SEM, but on a much smaller length scale (nanometer to angstrom). With this tool, morphology can be examined for individual phases comprising the IE-911 material (binder, CSTs, alteration phases, impurity phases). Furthermore, selected area EDS or electron diffraction gives compositional and crystallographic information on individual phases. DCP analysis gives bulk, quantitative chemical analysis on both solids and solutions used in various IE-911 treatment studies. IR spectroscopy was used to identify functional groups of potential adsorbants on CST surfaces (ligands and anions in the simulant solutions). This tool was especially useful for characterization of the batch simulant studies carried out at SRS. Finally, ^{29}Si solid state NMR was used to identify structural changes in the acid and sodium forms of CST by probing the silicon coordination environment.

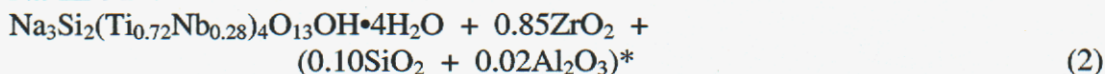
3.2 Characterization of H-IE-911 (as-received) and Na-IE-911 (pretreated)

The formulations of H-IE-911 (99-7, 99-9) and Na-IE-911 (99-7) were interpreted by the combined characterization methods as:

H-IE-911:



Na-IE-911:



**reacted in-situ to form an aluminosilicate*

$^\ddagger\text{IPX}$ = impurity phase X

The bulk composition of as-received IE-911 (99-7, 99-9) and NaOH pretreated IE-911 (99-7) were determined by DCP and summarized in Table 1. The overall compositions of the two as-received lots are consistent. The molar ratio of binder oxide to CST formula unit is approximately 1:1.

Table 1. DCP Analyses of As-received and NaOH Pretreated IE-911

Sample ID	wt % Ti	wt % Si	wt % Nb	wt % Na	wt % Zr	Nb occupancy	Ti occupancy	Mol % excess SiO ₂
IE-911 UOP batch 99-7; as received	16.48	7.69	12.64	3.52	9.34	0.28	0.72	12.8
IE-911 UOP batch 99-7; pretreated	17.83	8.26	12.61	10.00	9.57	0.27	0.73	14.08
IE-911 UOP batch 99-9; as received	16.67	7.46	12.28	3.80	10.09	0.28	0.72	10.01

Crystalline Silicotitanate Composition. The CSTs have the expected Ti:Nb ratio of ~3:1, where Nb substitutes into 1 of 4 coordination sites in the tetranuclear, octahedral cluster within the CST framework.⁸ Two of the three exchange sites in the as-received IE-911 are occupied by H⁺, which is an artifact of the acidic binding process. The third site is not easily exchanged due to its crystallographic location in the framework wall⁸⁻⁹ and remains occupied by sodium, despite the acidic binding process. In addition to elemental analysis, the H-IE-911 and Na-IE-911 forms were identified by XRPD and ²⁹Si solid state NMR. Figure 1 shows the XRPD spectra of H-IE-911 and Na-IE-911 (99-7). Both

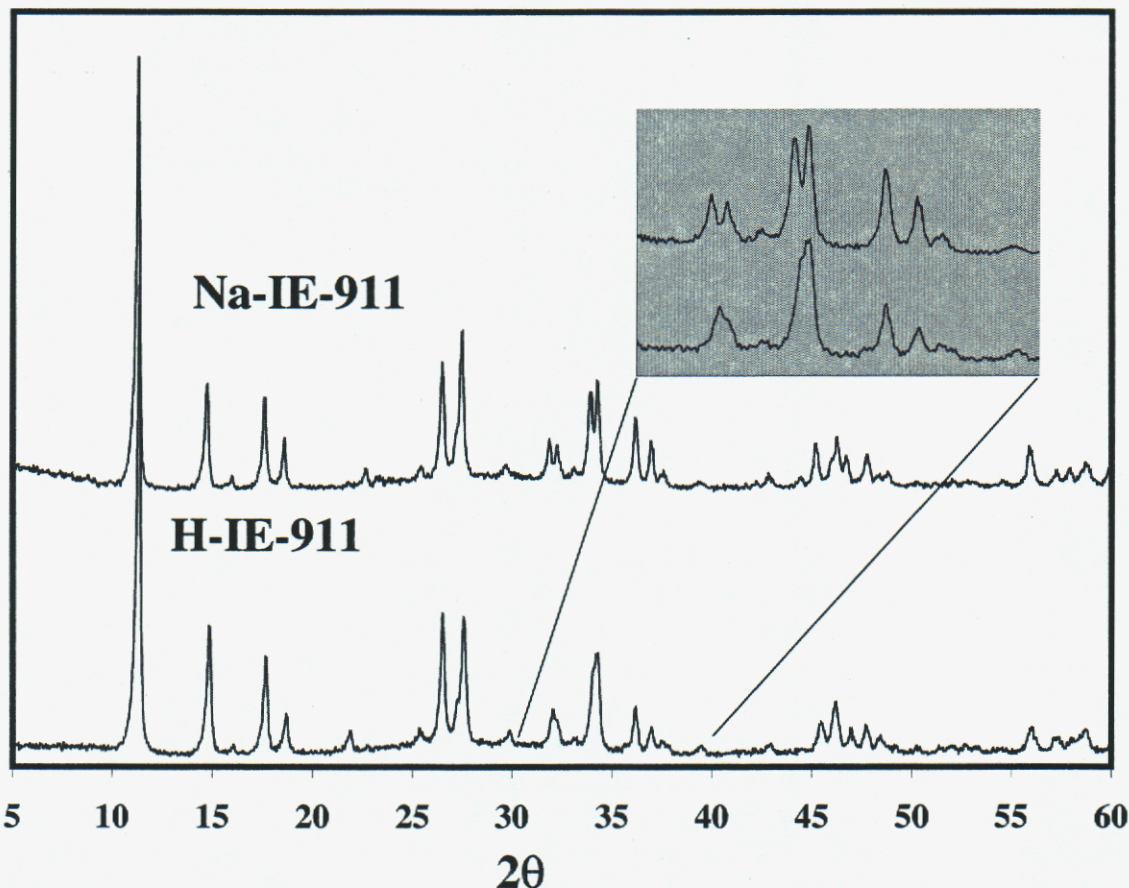


Figure 1. XRPD of as-received (H) and pretreated (Na) IE-911 emphasizing major differences between the two diffraction patterns in the region of $2\theta = 30 - 40^\circ$.

spectra show well-crystallized CST with no evidence of crystalline impurities. The major difference between the two diffraction spectra is observed in the peaks $2\theta = 32^\circ$ and $2\theta = 34^\circ$. In the H-IE-911 spectrum, these peaks are each broad singlets. In the Na-IE-911 spectrum, these peaks are each sharp doublets. An identical change is observed in the single-crystal data of the Na-CST and powder Rietveld refinement data of the H-CST of the pure Ti (no Nb) form of CST.⁹ Differences between H-IE-911 and Na-IE-911 were also characterized by solid state ^{29}Si NMR. The spectra of the two IE-911 forms are shown in Figure 2. The H-IE-911 (as received) has a single peak at -93 ppm and the Na-IE-911 (pretreated) has a single peak at -84 ppm. The single peak observed in each form represents a single, unique SiO_4 tetrahedral coordination environment for silicon in CST, which is in agreement with the crystallographically-determined structure.⁸ The shift in peak position from the H- to Na-IE-911 form represents small changes in the SiO_4 coordination environment (slight shifts in bond lengths and bond angles) in response to exchanging acid for sodium. An analogous ^{29}Si NMR shift was observed for the pure Ti (no Nb) CST material.⁹

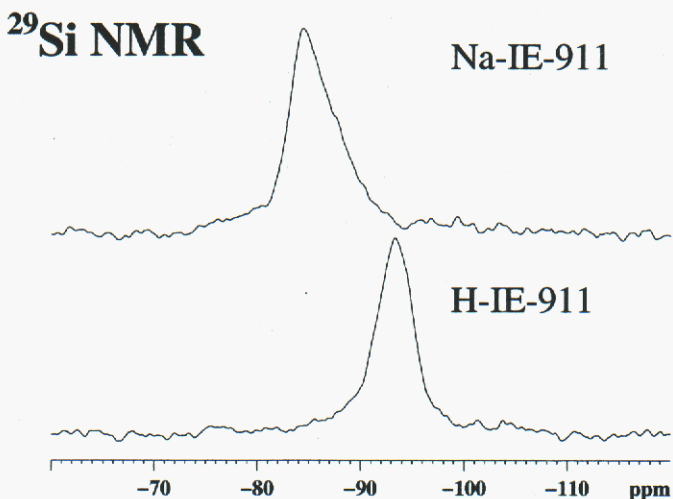


Figure 2. ^{29}Si NMR spectra of as received (H-IE-911) and pretreated (Na-IE-911) showing a single Si coordination environment for each form of CST. The peak shift results from slight alterations (bond angles and lengths) of the SiO_4 tetrahedron as a result of exchanging H for Na.

Impurity phases. The silica, alumina and IPX (impurity phase X) were not identifiable by XRPD, due to their poor crystallinity (silica and alumina) or low concentration (IPX). All three phases were identified by TEM, and the relative abundance of these three impurity phases were also estimated by TEM. Further evidence for excess silica was also seen in the DCP analysis, where the Si:(Ti+Nb) ratio is fixed by the CST formula. The TEM image in Figure 3 shows the silica and alumina impurities, which were identified by EDS. The silica and alumina are almost always aggregated together in ~ 50 nm, amorphous particles within the binder matrix. In the pre-treated IE-911, the alumina and silica are reacted with NaOH in-situ to form a sodium aluminosilicate phase. The third impurity phase, IPX, composes approximately 3-4 vol. % of the IE-911 and is viewed in a TEM image in Figure 4. It is a crystalline phase with a rod-like morphology, and is

identified as a niobium titanate phase by EDS analysis. This phase is not stable in the electron beam, which suggests it is a hydrated phase. Electron diffraction identified d-spacings of 13.6, 11.4, 9.54, and 8.63 Å for this phase, which is not consistent with any previously known niobium titanate phases in the JCPDS, NIST or ICSD data bases. This phase has been noted as a byproduct of CST synthesis since niobium was first introduced into the CST framework at Sandia National Laboratories¹⁰ and Texas A&M University.¹¹ This phase is currently under investigation as a possible source of the column plug that formed during column conditioning at SRS.² It is suspect because preliminary studies show it is solubilized when treated successively with an acid followed by a base.

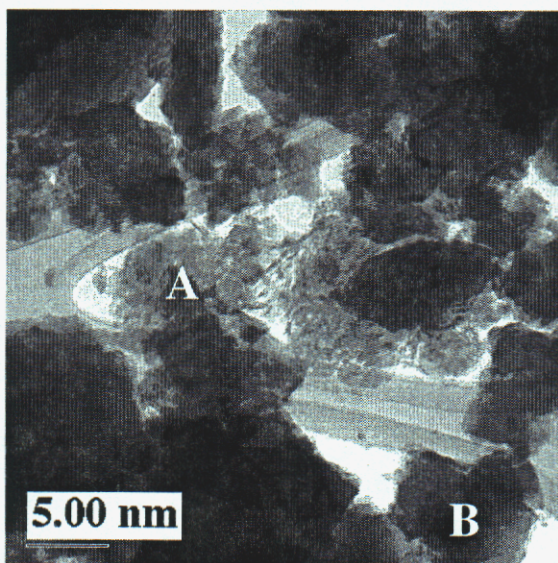


Figure 3. TEM image of as-received IE-911 showing 1) Amorphous silica impurity comprising ~10 volume % of as-received material (light area labeled 'A'); and 2) CST cube-shaped crystals agglomerated with zirconia binder (dark area labeled 'B').

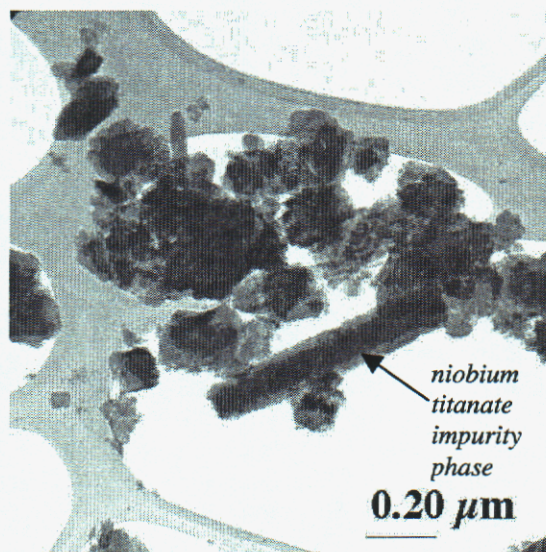


Figure 4. TEM image of as-received IE-911 showing rod-shaped, niobium titanate impurity which comprises ~ 3-4 volume % of the material.

Morphologies. SEM images of as-received and NaOH treated IE-911 (batch 99-7, pretreated at ORNL) are shown in Figure 5. The H-IE-911 pellets are irregular shaped, approximately 300-500 μm in diameter with smooth, featureless surfaces. The Na-IE-911 pellet surfaces are cracked and exfoliating. This is a morphology that is consistently observed throughout all the NaOH-treated and simulant-treated samples, and will be discussed further in the next section. The TEM image of H-IE-911 is shown in Figure 6a. It is composed of 100-200 nm cube-shaped crystals of tetragonal CST. The binder material appears as irregular-shaped particles cemented onto the CST crystals. The TEM image of NaOH-treated IE-911 shown in Figure 6b reveals an "aggregated" texture in approximately 25 vol. % of the material. Although the morphology is different in appearance from the as-received IE-911, there is no significant composition change (except for increased Na), as determined by EDS. This aggregated texture is consistent with the cracking and exfoliation morphology observed in the intact Na-IE-911 by SEM.

That is, the aggregated material observed by TEM may be a brittle shell on the IE-911 pellets, formed during NaOH-pretreatment. Furthermore, this brittle shell may crack and exfoliate in response to pellet shrinking or swelling as result of numerous processes including wetting and drying of the IE-911.

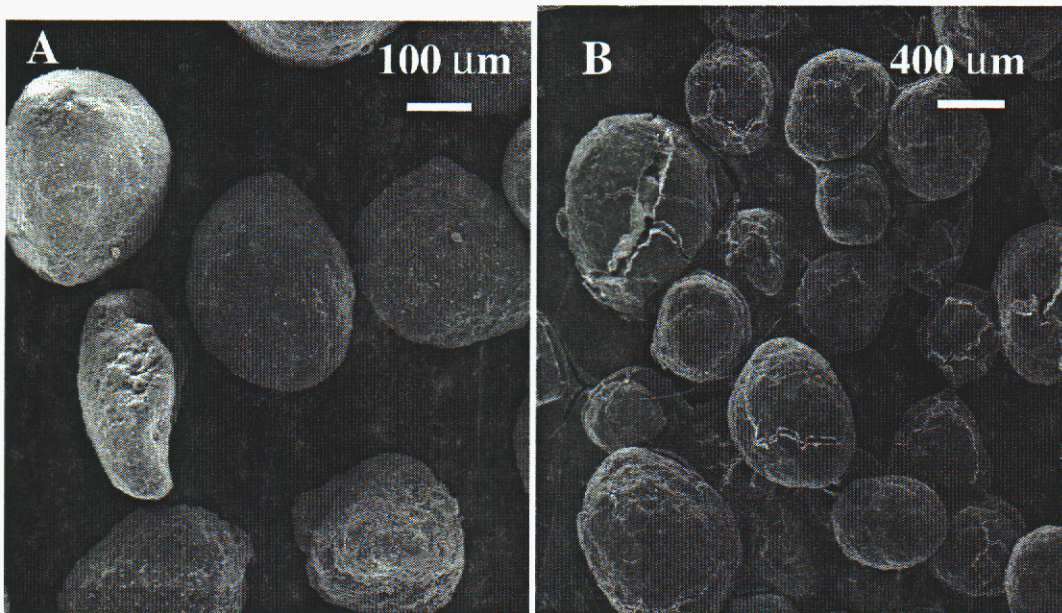


Figure 5. SEM images comparing morphologies of as-received (A) and NaOH-treated (B) IE-911. As received IE-911 pellets have smooth, featureless surfaces. NaOH-treated IE-911 shows cracking/exfoliation morphology.

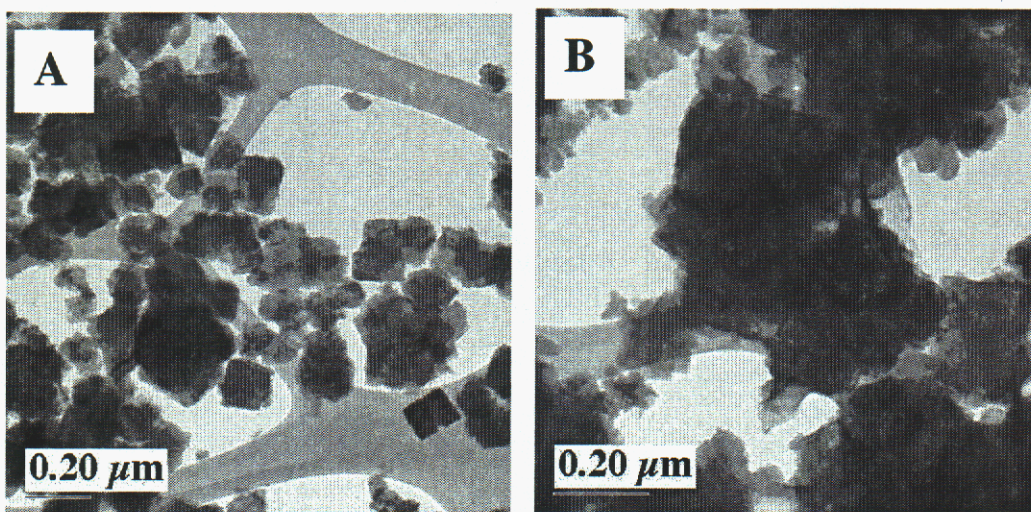


Figure 6. TEM images of as-received (A) and NaOH-treated (B) IE-911. As-received IE-911 shows cube-shaped CST crystals with agglomerated binder. The NaOH-treated IE-911 shows an overgrowth morphology in approximately 25 volume %, which may be responsible for the cracking / exfoliation morphology observed by SEM.

3.3 Batch Simulant Studies

ORNL temperature studies.

Taylor and Mattus⁴ studied IE-911 performance as a function of simulant temperature, using the aluminum-containing average salt simulant. The characterization results for these samples are summarized in Appendix A, Table A-1. The main conclusions drawn from characterization of these samples include:

- The simulant-treated IE-911 samples treated from 23-80 °C remain largely intact and unaltered.
- The CST material of the simulant-treated IE-911 exposed at 120 °C is mostly decomposed to three different alteration phases
- An aluminosilicate phase deposited on the IE-911 pellet surfaces is identified as cancrinite, $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (JCPDS # 38-513).
- Increased temperature of simulant exposure results in increased cancrinite formation.
- The cracking/exfoliation first seen in the NaOH-treated samples is also observed in this suite of samples.
- Increased temperature of simulant exposure results in advancement of the cracking/exfoliation.

The XRPD spectra of heat-treated IE-911 (batch 98-5) are shown in Figure 7, along with the XRPD spectrum of NaOH-treated IE-911 for reference. In the 23-80 °C simulant treated samples, small peaks at $2\theta = 14^\circ$ and $2\theta = 24^\circ$ increase in intensity with increasing temperature of simulant treatment. These are the main peaks of the cancrinite Na aluminosilicate phase. However, the bulk of the CST material remains largely unaltered. Bulk elemental analysis of these samples support this observation that the CSTs remain largely intact up to 80 °C. The elemental compositions of the simulant-exposed IE-911 samples at 23, 50, 80, and 120 °C, along with NaOH-pretreated IE-911 are compiled in Table 2. For the NaOH-treated and 23-80 °C simulant treated samples, there are no observed trends of increased or decreased wt % for any elements. However, within these four samples, the wt % Na, Si, Ti, Nb, and Zr varies from $\Delta 1.2\%$ (Si) to $\Delta 4.2\%$ (Nb). Since the variations do not vary directly as a function of temperature of simulant exposure, it is likely they arise from experimental uncertainty. The biggest uncertainty is likely to be introduced in weighing the very small (5-10 mg) solid sample for digestion in solution for DCP analysis. In the weighing of such small samples, uncertainty is introduced in static effects and fluctuating sample moisture content. Although this uncertainty introduces inaccuracies in determination of absolute metal concentrations, it is canceled out in determination of metal ratios within a given sample.

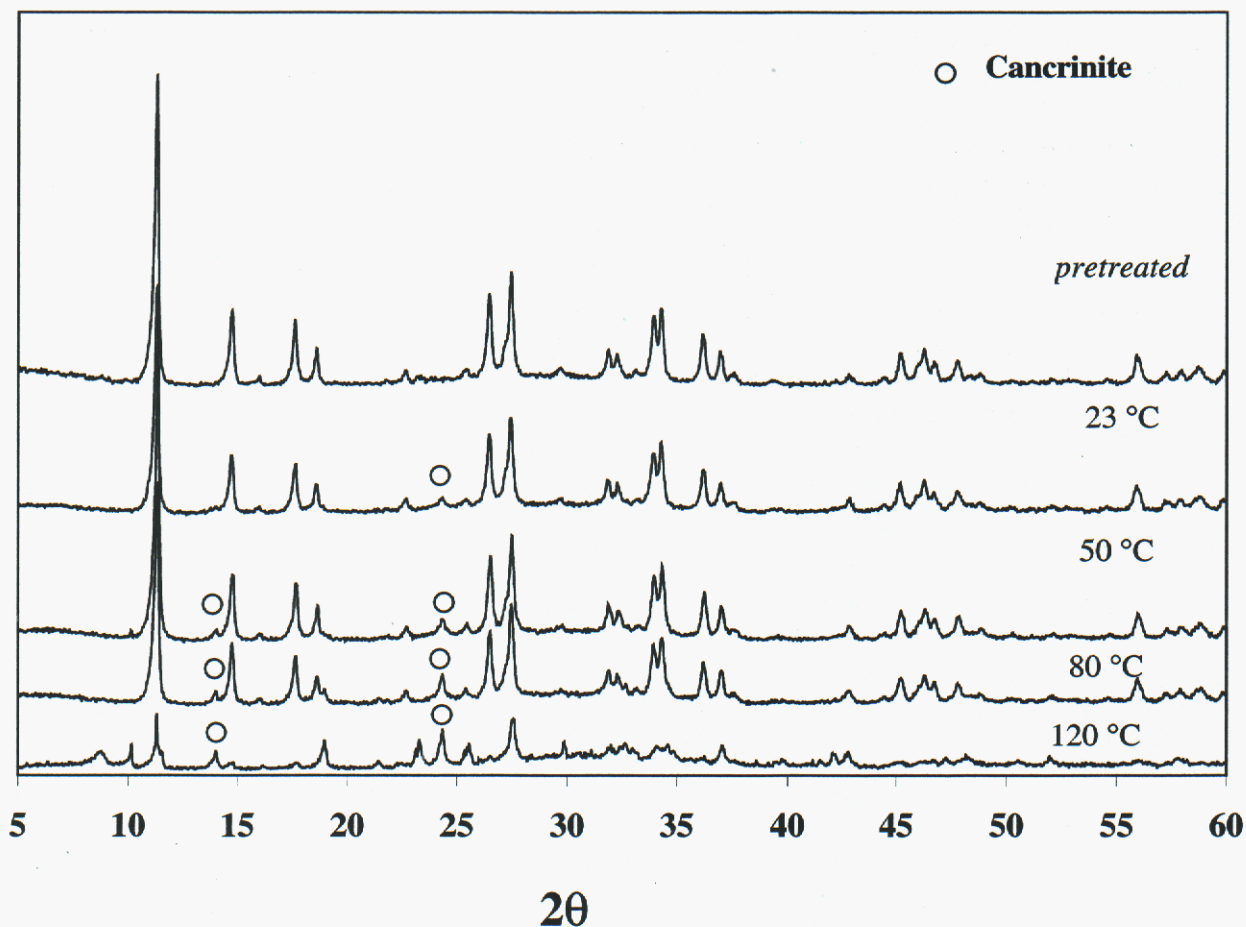


Figure 7. XRPD spectra of simulant-heat treated IE-911 showing; 1) The CSTs remain largely intact up to 80 °C treatment, 2) Cancrinite ($\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) deposition increases with increasing temperature treatment, and 3) CST is almost completely decomposed with 120 °C simulant treatment.

Table 2. DCP Analysis of Temperature-Simulant Treated IE-911

Temperature of simulant treatment	Cs K _α	wt % Na	wt % Si	wt % Ti	wt % Nb	wt % Zr
NaOH-pretreated	1200	10.0	8.3	17.8	12.6	9.6
23 °C	860	11.3	8.6	14.3	14.8	8.8
50 °C	692	13.0	9.5	17.8	16.8	10.4
80 °C	644	10.9	8.5	15.6	13.6	8.5
120 °C	47	17.2	4.8	9.3	7.7	5.3

SEM images of the simulant/heat exposed IE-911 show increasing coverage of the pellet surfaces by cancrinite with increasing temperature. For instance, Figure 8 shows a close-up view of the simulant-exposed IE-911 at 23 °C (8a) and 50 °C (8b). With 23 °C simulant exposure, isolated, spherical, ~2 μm growths composed of Si, Al and Na (EDS

analysis) are observed on the pellet surfaces. With 50 °C simulant exposure, the spherical cancrinite growths form a continuous layer with increased thickness on the pellet surfaces. EDS analyses of the surfaces shows, increasing concentration of cancrinite metals (Al and Si) and decreasing concentration of IE-911 metals (Ti, Zr, Nb) with increasing temperature of treatment.

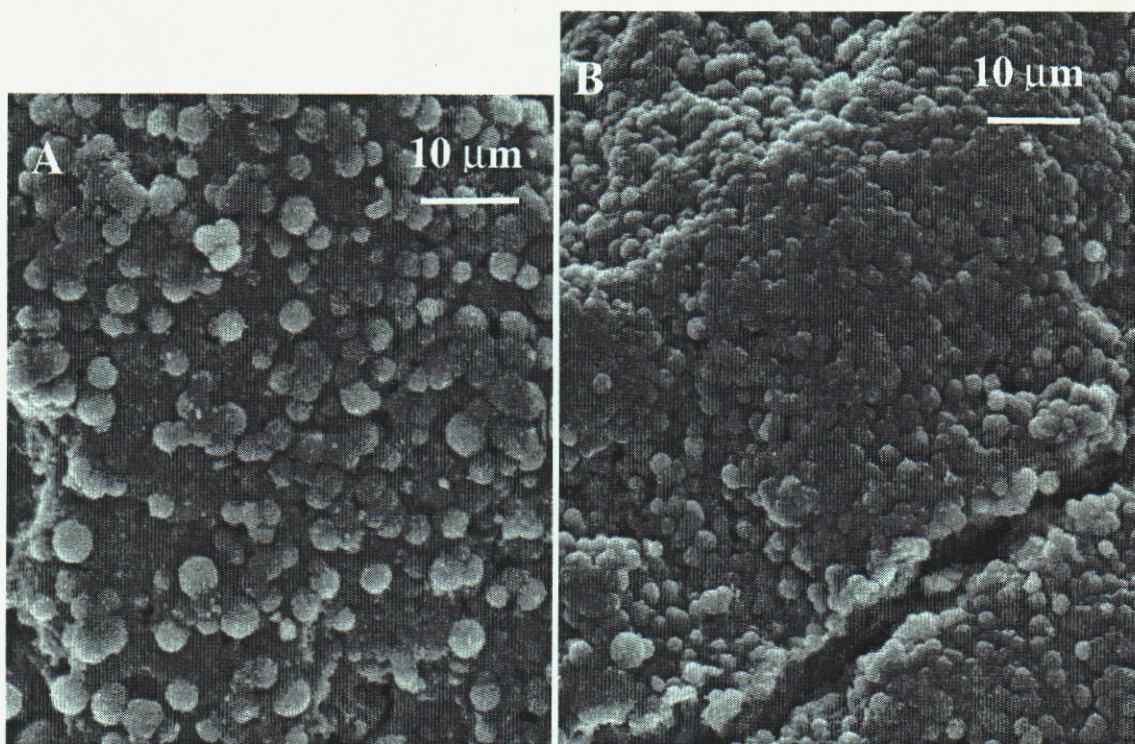


Figure 8. Surfaces of temperature-simulant treated IE-911 (A= 23 °C; B = 50 °C treatment). Isolated, spherical deposits of cancrinite are observed in the 23 °C-treated sample, which become a continuous, thick layer on the 50 °C-treated sample.

Also with increasing temperature of simulant exposure, increasing **exfoliation/cracking** is observed. As the temperature of simulant exposure increases, this morphology advances from 1) predominantly round pellets with deep surface cracks in what appears to be a brittle surface layer; to 2) increasing irregular-shaped pellets and appearance of fines formed by the surface layer flaking off the pellets. These morphologies are observed in Figures 9a (50 °C) and 9b (80 °C). By EDS analyses, these fines have varying composition; either rich in IE-911 metals or rich in Na aluminosilicate metals. This observation suggests that while cancrinite deposition can certainly contribute to the formation of brittle surface coverage on the pellets, there is an independent, surface morphology-alteration process that results in exfoliation. Furthermore, this process takes place without significantly altering the IE-911 surface composition. This conclusion is supported by the fact that both 1) NaOH-pretreated IE-911 and 2) IE-911 exposed to

aluminum-free simulants (discussed below) also show the surface exfoliation, without any evidence for aluminosilicate deposition.

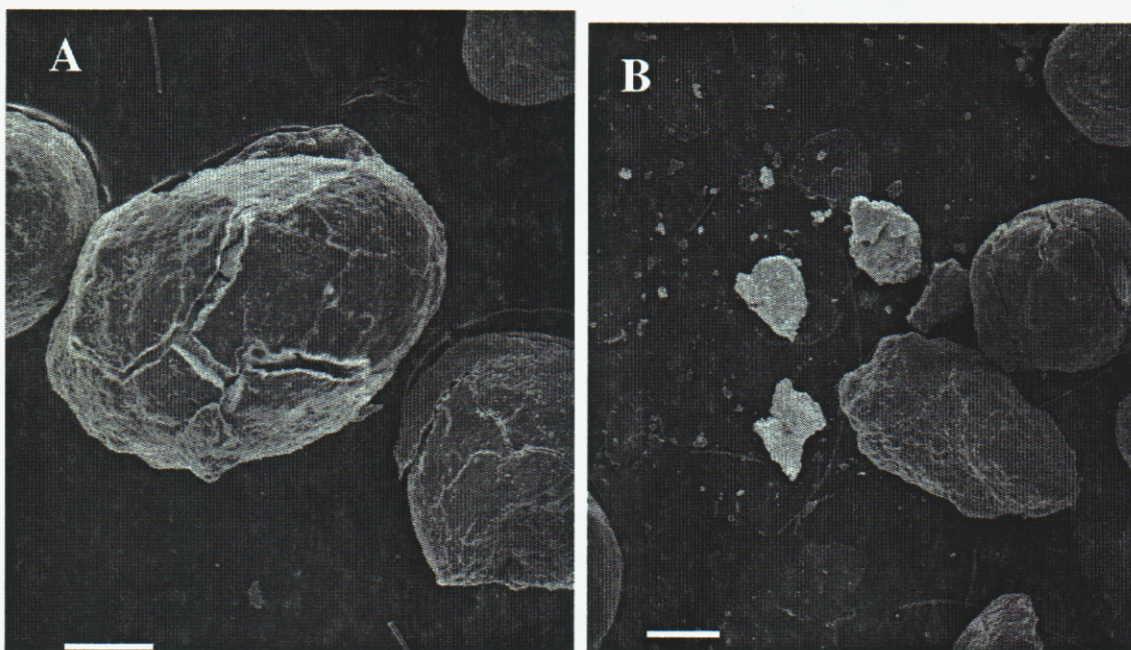


Figure 9. IE-911 treated at 50 °C (A) and 80 °C (B) in average simulant solution showing advancing in cracking/exfoliation. With increasing temperature of treatment, pellets become irregular-shaped with exfoliation of surface layers.

The XRPD spectrum and two SEM images of 120 °C simulant-exposed IE-911 are shown in figures 10a, b and c. The diffraction peaks (10c) of the CSTs are much diminished. The diffraction pattern is dominated by three alterations phases; 1) the $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ cancrinite phase, 2) $\text{Na}_7(\text{H}_3\text{O})\text{Nb}_6\text{O}_{19} \cdot 14\text{H}_2\text{O}$ hexaniobate phase (JCPDF #84-188), and 3) $\text{Na}_3\text{SO}_4\text{F}$ (JCPDF #15-678).

The hexaniobate phase is observed in figure 10a as $15 \times 100 \mu\text{m}$ rods. Figure 10b shows very large (observable by naked eye) crystals of the sodium sulfate halide phase, overgrowing several pellets. Almost complete destruction of the CST phase is likely responsible for the extreme $\text{Cs } K_d$ drop (47 ml/g; see Appendix A, Table A-1) observed for this sample.

Two additional simulant-temperature treated IE-911 samples were sent from ORNL; 23 and 80 °C/ 5 months (Table A-1). The sample treated at 80 °C/ 5 months has a significant K_d drop (740 ml/g). The XRPD spectrum reveals the CSTs are predominantly unaltered with some cancrinite precipitate. These diffraction patterns are shown in Appendix B.

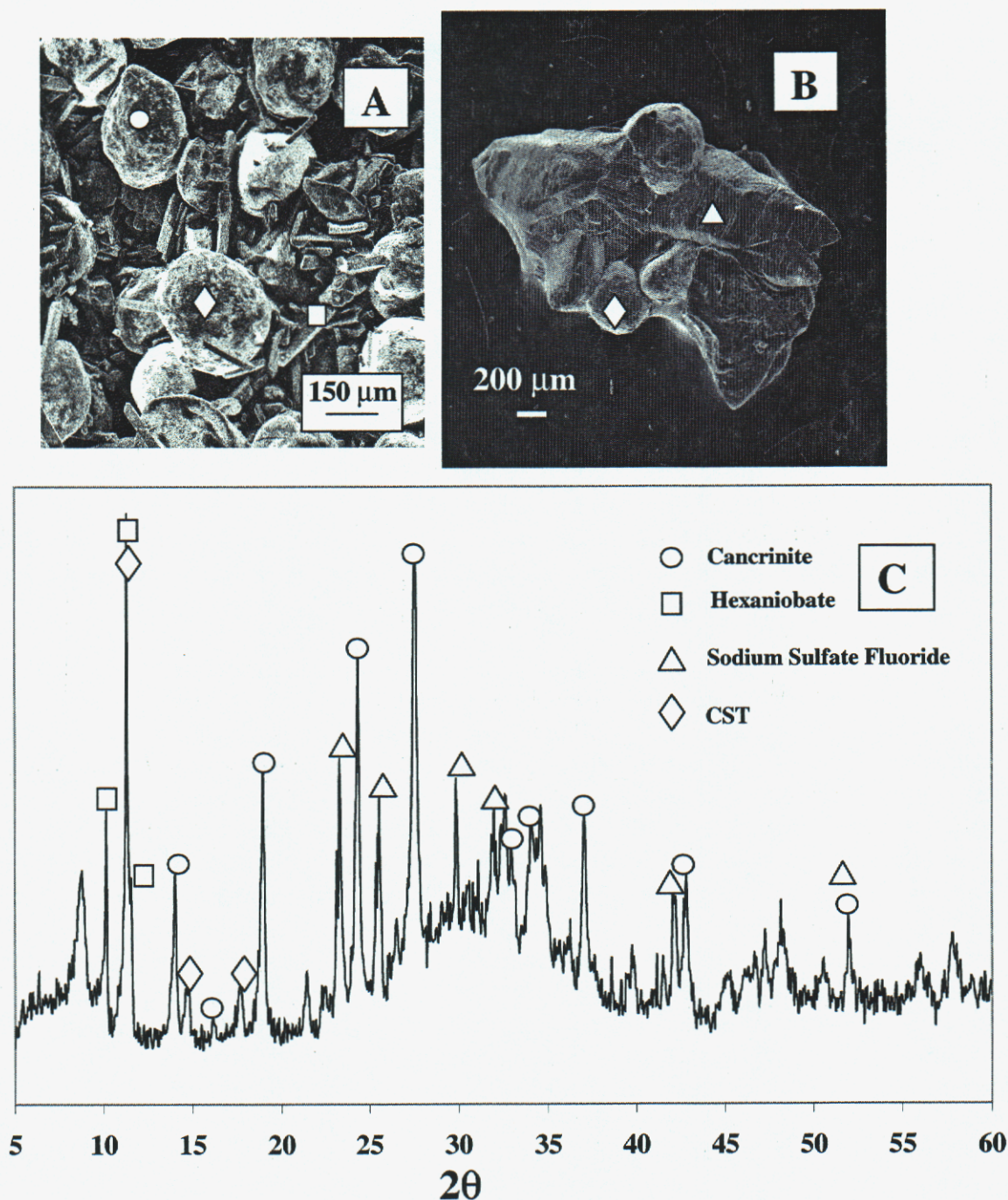


Figure 10. Characterization of 120 °C treated IE-911. (A) SEM image showing hexaniobate crystals and pellets with cancrinite precipitate. (B) SEM image showing large sodium sulfate fluoride crystals enveloping IE-911 pellets. (C) XRPD spectrum with identifying peaks of alteration phases marked.

SRS simulant composition studies.

A series of experiments were carried out at SRS to determine the stability of IE-911 (UOP batch 99-9) in various simulant compositions.⁷ The sample descriptions and characterization highlights are summarized in **Appendix A**, Table A-2. XRPD

diffraction spectra are compiled in **Appendix B**. Major conclusions from this suite of samples include:

- NaOH-pretreated and simulant treated IE-911 samples exhibit the same cracking and exfoliation morphology observed in the ORNL samples.
- Alumina-containing simulants produced cancrinite precipitates on IE-911 pellet surfaces; non-alumina simulants did not produce cancrinite precipitates.
- The $\text{C}_2\text{O}_4^{2-}$ and CO_3^{2-} anions added to average simulant solution do not adsorb onto the surface or pores of the CSTs.
- The H_2O_2 added to average simulant solution results in partial decomposition of the CSTs.

Figure 11 shows as-received IE-911 and NaOH-treated IE-911, each treated at room temperature with distilled water for two months. Similar to the as-received and NaOH-treated IE-911 from ORNL, the as-received sample is featureless pellets, and the NaOH-treated sample shows extensive cracking and exfoliation. EDS analysis shows normal H-IE-911 and Na-IE-911 compositions, respectively. These observations are typical and representative of the suite of simulant-treated samples.

The only simulant-treated sample from SRS that showed significant alteration is that which was exposed to hydrogen peroxide (see Appendix A, table A-2). The sample was light yellow in appearance, and grinding of this sample in a CsI matrix resulted in bright yellow coloration. Hydrogen peroxide notoriously coordinates titanium and forms soluble, yellow-colored species in solution. Consequently, extensive treatment of titanium oxides with H_2O_2 results in decomposition of the oxide framework. Figure 12 shows the XRPD spectrum of IE-911 exposed to average salt simulant with added H_2O_2 . The peak at $2\theta = 9^\circ$ is indicative of formation of a decomposition phase of IE-911.

Infrared Spectroscopy (IR) was used for the SRS suite of samples to determine if the $\text{H}_2\text{O}_2^{2-}$, $\text{C}_2\text{O}_4^{2-}$ or CO_3 species adsorb into the pores or surface of CST, which can consequently result in inhibition of ion exchange or sorption. Figure 13 shows the IR spectra of IE-911 samples treated with average salt simulant, containing these three anions. IE-910 (no binder), as-received IE-911 and pretreated IE-911 are also shown for reference. Several results are revealed from this study. [It is observed that the binder does not contribute any significant peaks to the IR spectrum] The spectra of IE-911 exposed to average salt simulant with added H_2O_2 , $\text{C}_2\text{O}_4^{2-}$ or CO_3^{2-} all have differences from the reference spectrum (pretreated IE-911), but they all differ in the same manner. Each of the above-mentioned spectra have additional peaks at 1360 and 1560 cm^{-1} , as compared to the pretreated IE-911. Therefore these peaks are likely to be a result of some reaction with a simulant component other than H_2O_2 , $\text{C}_2\text{O}_4^{2-}$ or CO_3^{2-} . At this point, we have no conclusive evidence for the identity of these peaks. Two reasonable possibilities are: 1) These peaks belong to a nitrate, due to precipitation of sodium nitrate on the pellet surfaces. 2) These peaks are a result of change in water/OH content of the CSTs pores. However, the main conclusion is, there is no evidence for adsorption of these species into CST pores.

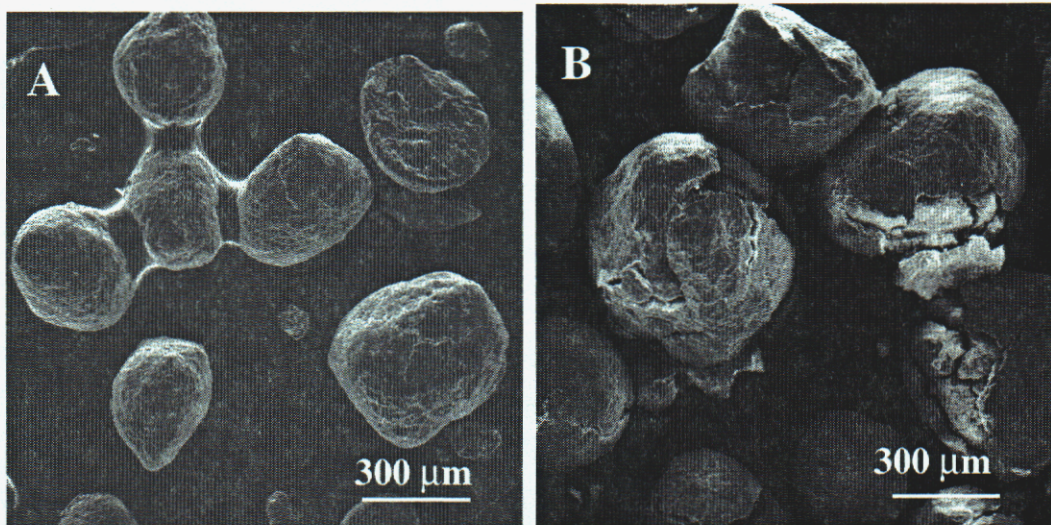


Figure 11. As received (A) and NaOH-pretreated IE-911 soaked in DI water for 2 months at room temperature. The NaOH-pretreated IE-911 exhibits extensive cracking/exfoliation morphology.

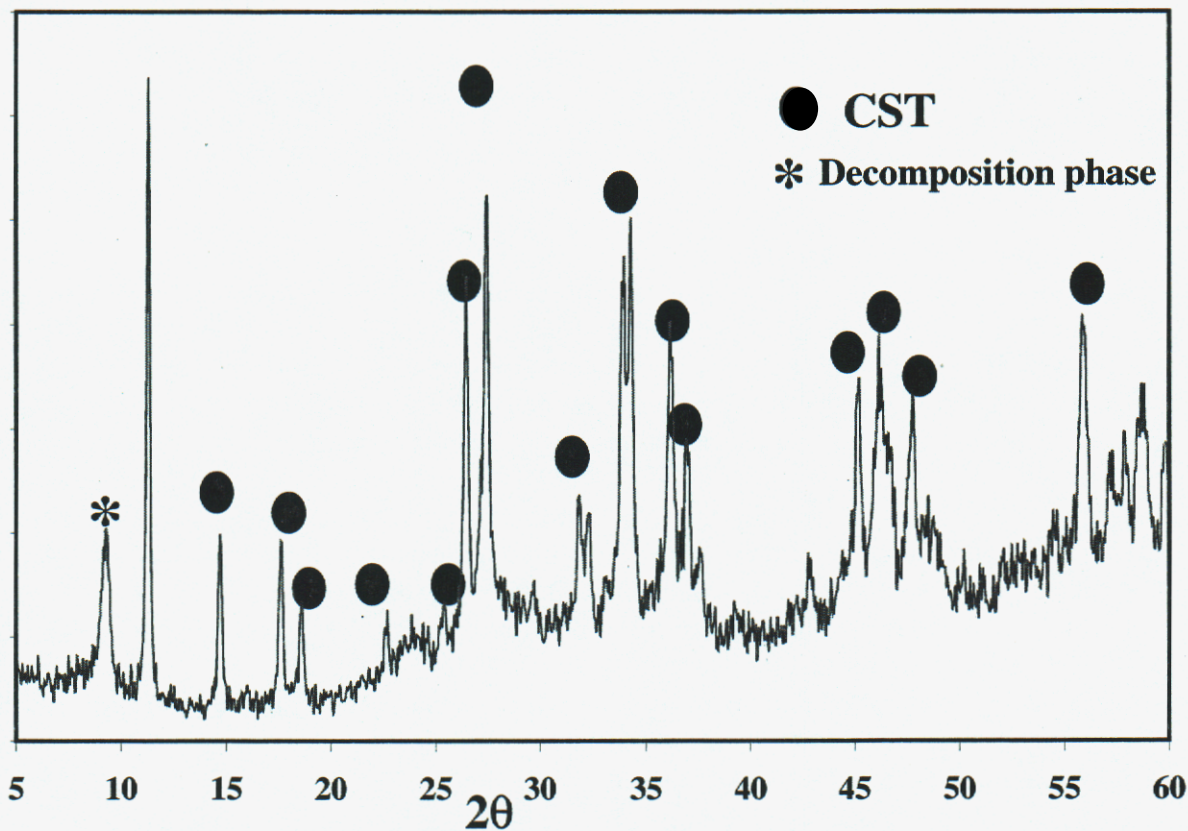


Figure 12. XRPD spectrum of IE-911 treated with average simulant solution with added H_2O_2 . The starred peak is an alteration phase resulting from decomposition of the CSTs via H_2O_2 complexation and extraction of the titanium from the CST framework.

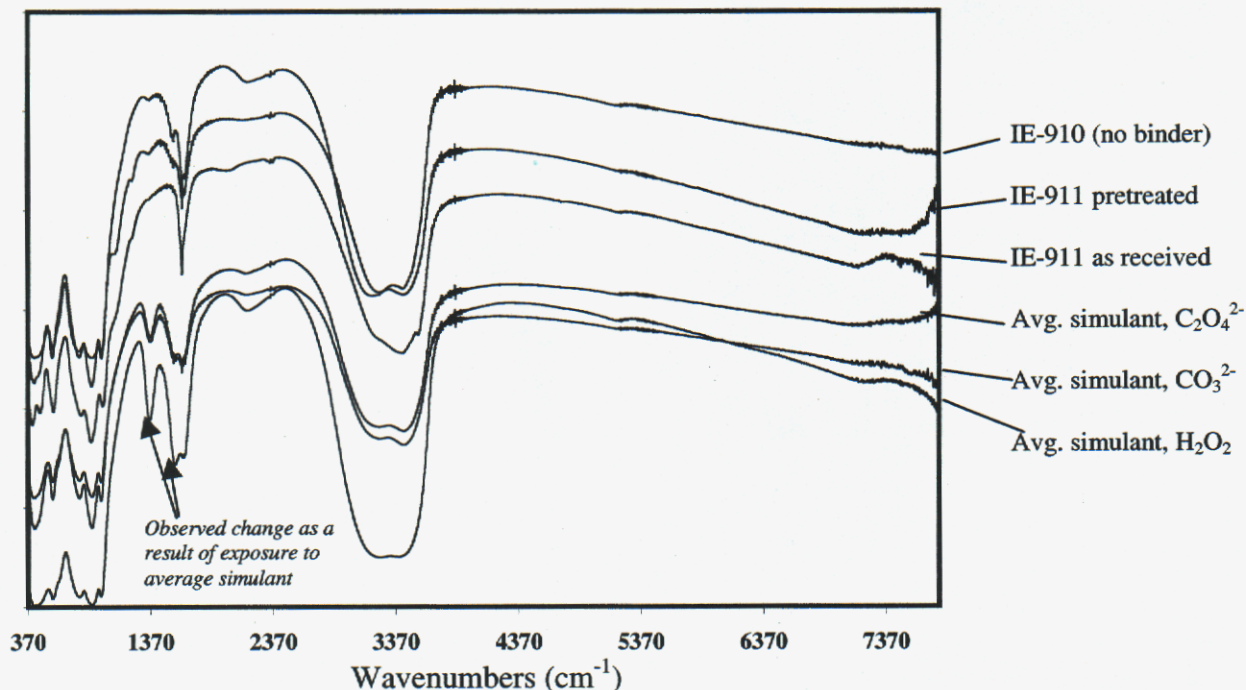


Figure 13. Infrared spectra of simulant-treated IE-911 samples. The peaks from ~300-1000 wavenumbers are metal-oxygen bond vibrations. The peaks above 1000 wavenumbers are hydrogen-oxygen bond vibrations of lattice water and hydroxyls. The marked peaks are nitrate or water vibrations. No effect on the CST framework of the H_2O_2 , CO_3^{2-} or $\text{C}_2\text{O}_4^{2-}$ are observed.

3.4 Column Studies (ORNL)

A series of IE-911 samples from recirculating columns of 1) average simulant (aluminum-containing) and 2) high pH-salt simulant (aluminum-free) were also received from ORNL⁴. The XRPD spectra of this suite of samples is compiled in Appendix B. These IE-911 samples (UOP batch 98-5, pretreated) were removed from the middle of the column at 1, 2, 3, 4, 4.5 and 5 months. Major results from this series of experiments includes:

- IE-911 in column of recirculating average simulant has a slight K_d drop from ~1200 ml/g to ~1000 ml/g with increasing time in the column.
- Increasing time in recirculating average simulant results in increasing formation of cancrinite on pellet surface.
- IE-911 in column of recirculating high pH salt simulant does not show K_d drop with increasing time, and no cancrinite formation.
- Both series of samples show cracking/exfoliation.
- Cancrinite deposition occurs mainly on the pellet surfaces and not throughout the core of the pellets.

SEM images of the 1, 3 and 5 month column-treated samples in 1) average simulant and 2) high pH salt simulant are shown in Figures 14a and 14b, respectively. Both series show extensive cracking/exfoliation. An extensive core-rim morphology of the pellets is observed in the 5 month-average simulant sample. EDS analysis (compiled in Table 3) of the samples from the average simulant column show increasing Na, Al and Si and decreasing Ti, Nb and Zr on the pellet surfaces, which is indicative of increasing cancrinite deposition with time. Furthermore, EDS analysis of a surface that is exposed by exfoliation (Figure 15) of outer layers [Table 3, column 5] has decreased Al and Si. This suggests the aluminosilicate deposition is limited to exposed surfaces of the pellets, and does not take place extensively within the macropores of the binder-CST composite or the micropores of the CSTs. On the other hand, compositional analysis by EDS of the pellet surfaces from the high pH salt column show no significant change with increased time in the column. Furthermore, no drop in Cs K_d was noted.

Table 3. EDS* Analyses of Column-treated IE-911 Samples.

element	Average simulant				High pH salt simulant		
	1 month	3 months	5 months (surface)	5 months (core)	1 month	3 months	5 months**
Na (mol %)	2.2	4.4	22.6	27.8	2.2	2.5	0.6
Al (mol %)	5.0	18.1	30.5	5.5	0.1	0.4	0.3
Si (mol %)	16.0	28.7	26.7	18.0	11.0	10.8	5.8
Ti (mol %)	59.9	40.4	19.2	27.9	68.3	67.0	80.2
Nb (mol %)	12.3	6.5	0.36	11.4	12.3	11.6	8.1
Zr (mol %)	4.6	1.9	0.65	9.4	6.0	7.7	5.0

*Although EDS data is not quantitatively accurate due to sample surface effects, observed trends are accurate since the error introduced by surface roughness is equivalent for samples with similar morphology.

** The anomalous values for Ti (high) and Si, Nb and Zr (low) for the high pH salt-5 month sample is currently under investigation.

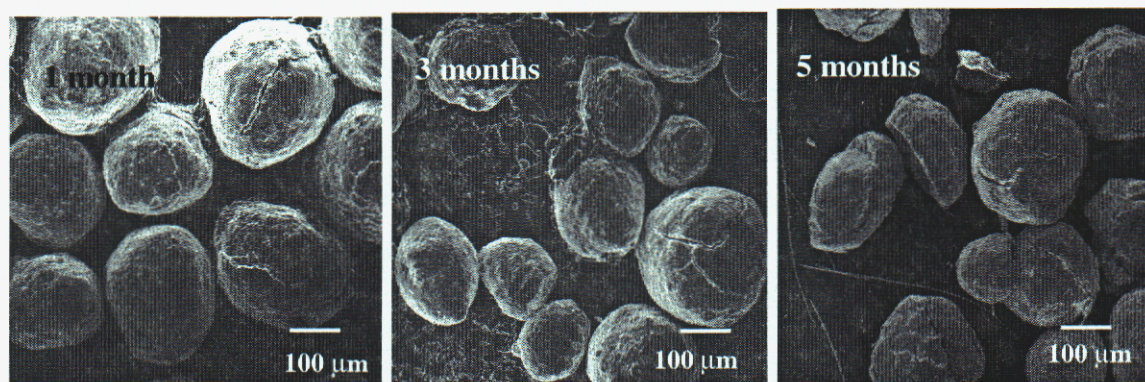


Figure 14a. IE-911 in average simulant recirculating column at room temperature for 1-5 months. Pellet surfaces show extensive cracking/exfoliation features, as well as increased aluminosilicate deposition with time (not observable at this scale; see Table 3).

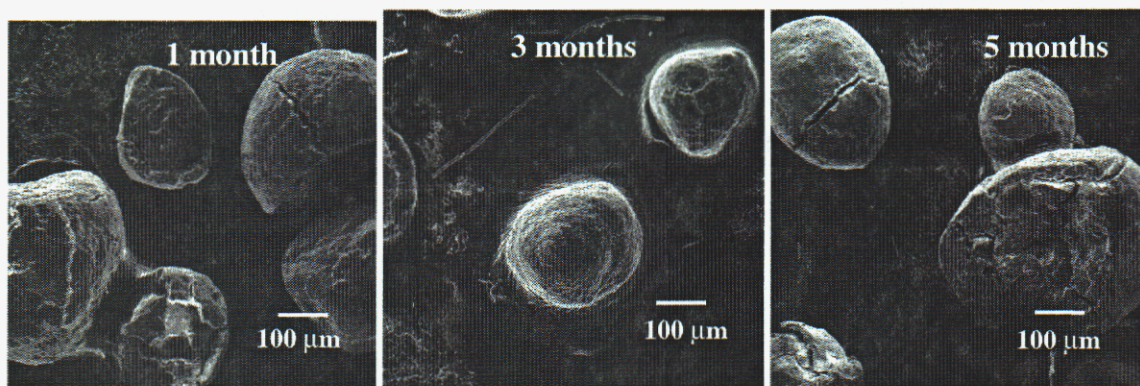


Figure 14b. IE-911 in high pH salt recirculating column at room temperature for 1-5 months. Pellet surfaces show extensive cracking/exfoliation features. No aluminosilicate deposition is observed on the pellet surfaces (see Table 3).

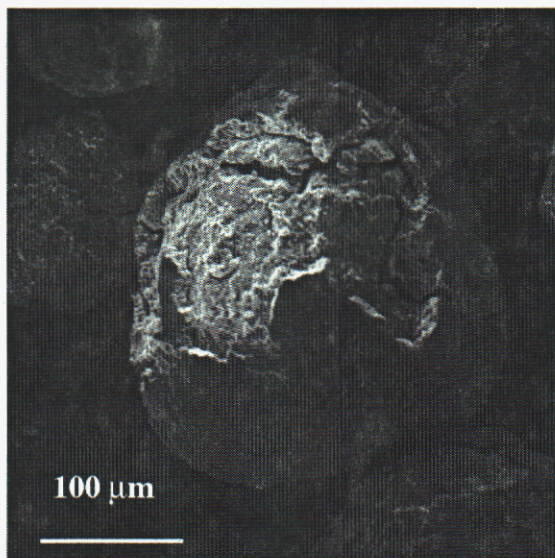


Figure 15. SEM image of an exfoliating IE-911 pellet from 5 month treatment in a recirculating column of average salt solution. The outer surface has a higher Na/Al/ Si concentration than the exposed core (see Table 3).

Although SEM/EDS indicates an increase in cancrinite deposition on the pellet surfaces with increasing time in the average simulant column, XRPD reveals that the total amount of cancrinite deposited is quite minimal. This point is illustrated in Figure 16, where the XRPD spectra of IE-911 in average simulant and high pH salt simulant are compared.

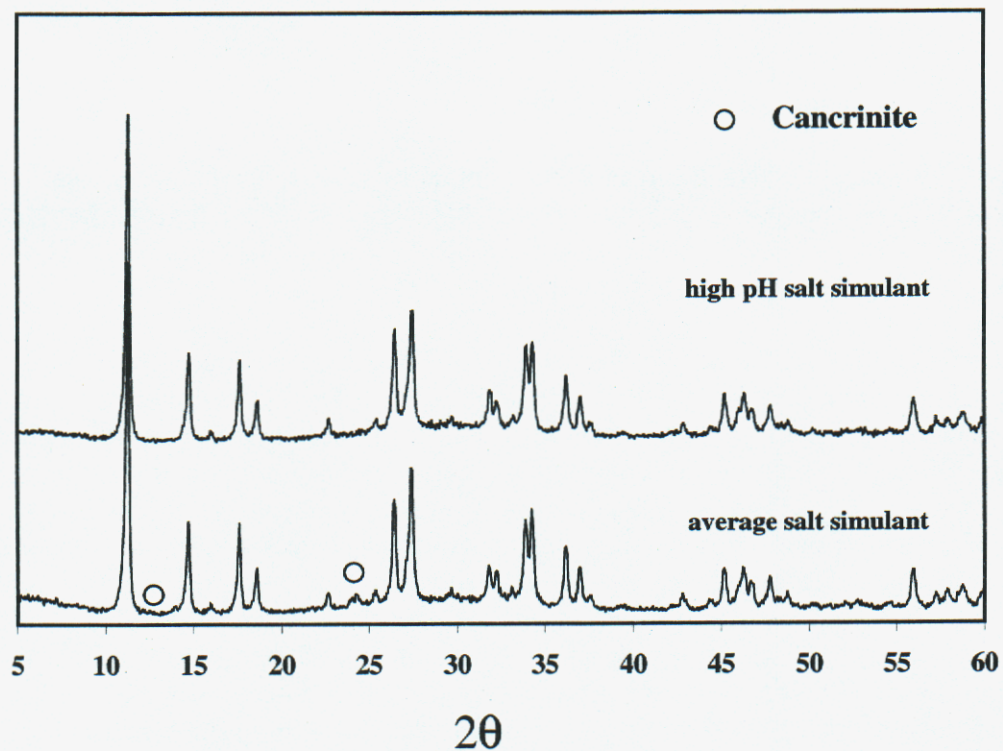


Figure 16. XRPD of IE-911 in recirculating columns of; 1) average salt simulant (alumina containing) and 2) high pH salt simulant (alumina free) at room temperature for 4.5 months. The deposition of cancrinite is minimal in the average salt simulant and non-existent in the high pH salt simulant.

4.0 Summary and Conclusions

A variety of as-received, NaOH-treated and simulant treated (from ORNL and SRS) samples of IE-911, the zirconia-bound form of crystalline silicotitanate, have been characterized by several techniques including XRPD, SEM/EDS, TEM/EDS, DCP and IR. These studies have revealed the following:

As-received IE-911 (UOP batches 99-7 and 99-9) is composed mainly of 1) well-crystallized, acidified CST with ~ 3:1 Ti:Nb ratio and 2) approximately 10 wt. % zirconia binder. These UOP batches also contain three minor impurity phases; amorphous silica (~10 volume %), amorphous alumina (~5 volume %) and a crystalline niobium titanate (~3 %). The crystalline niobium titanate is currently under investigation as a source of the Nb-oxide rich column plug, since it undergoes dissolution with certain solution treatments. The morphology of the as-received pellets is smooth and featureless.

NaOH pretreated IE-911 is composed of the Na-form of CST and binder. The overall composition of IE-911 does not vary significantly from the pretreatment, except for the increase in sodium content. However, the silica and alumina impurities react in-situ to form a sodium aluminosilicate phase. We are currently investigating the fate of the niobium titanate phase as a result of this pre-treatment. The morphology of the pellet surfaces is cracked and exfoliating.

Simulant treated IE-911 pellets all have cracked and exfoliating morphologies, regardless of the composition of the simulant in which they were treated. However, K_d performance is not impacted by these morphology changes. Samples treated in aluminum-containing simulant (average salt simulant) all have cancrinite precipitated on the pellet surfaces. This precipitation increases in density, thickness and continuity with increasing temperature or time of simulant exposure. This deposition occurs in both column and batch tests. However, the bulk of the IE-911 material remains unaltered by simulant treatment, up to 80 °C exposure temperature for 86 days. Furthermore, cancrinite deposition is limited to the pellet surface, and does not penetrate the core of the pellets. A slight Cs K_d drop (Δ 200 ml/g over 5 months column exposure at room temperature) is correlated with increasing cancrinite deposition; that this, Cs K_d drop is not observed in similar tests using aluminum-free simulant. A more significant K_d drop is observed in the batch tests at elevated temperature, from 1200 ml/g (pretreated) to 644 ml/g (80 °C/86 days). Simulant exposure at 120 °C resulted in complete CST destruction.

Future work on this project includes: 1) Characterization of the short-term exposure samples recently received from PNNL, 2) Compile, compare and contrast the characterization data of simulant treated samples from SRS, ORNL and PNNL, 3) Determine the cause and mechanism of the cracking/exfoliation and evaluate its effect on material performance, 4) Confirm identity of the niobium titanate impurity as a source of Nb oxide plug formation and devise a recommendation for IE-911 treatment to avoid this plug formation phenomenon (in conjunction with J. Krumhansl).

5.0 Cited References

1. Walker, D. D. Interoffice memorandum # SRT-LWP-2000-00136: *Crystalline Silicotitanate Column Plugging Incidents*, Savannah River Site, Aiken, SC, August 22, 1999.
2. Walker, D. D. et al. # WSRC-TR-99-308: *Cesium Removal From Savannah River Site Radioactive Waste Using Crystalline Silicotitanate (IONSIV[®] IE-911)*, Savannah River Site, Aiken, SC, September 18, 1999.
3. Welch et al., # ORNL-TM-99-103: *Hydraulic Performance and Gas Behavior of Tall, Crystalline-Silicotitanate Ion-Exchange Column*, Oak Ridge National Laboratory, Oak Ridge, TN, October 1999.
4. Taylor, P. A. and Mattus, C. H. # ORNL-TM-99-233: *Thermal and Chemical Stability of Crystalline Silicotitanate Sorbent*, Oak Ridge National Laboratory, Oak Ridge, TN, October 1999.
5. Nenoff, T. M.; Thoma, S. G. and J. L. Krumhansl, # SAND-96-258: *The Stability and Selectivity of TAM5: A Silicotitanate Molecular Sieve for Radwaste Cleanup*, Sandia National Laboratories, Albuquerque, NM, November 1996.
6. Walker, D. D., # SRT-LWP-2000-0028: *Pretreatment Guidelines*, Savannah River Site, Aiken, SC 1999.
7. Fondeur, F. F., #WSRC-RP-99-00597: *The Effect of Pressure and Organic Constituents on the Cesium Ion Exchange Performance of IONSIV IE-911*, Savannah River Site, Aiken, SC, October, 1999.
8. Nenoff, T. M. and Krumhansl, J. L. #SAND96-2578: *The Structure of TAM-5: A Silicotitanate for Radwaste Clean-up*, Sandia National Laboratories, Albuquerque, NM, November 1999.
9. Poojary, D. M., Bortun, A. I., Bortun, L. N. and Clearfield, A. *Inorg. Chem.*, 1996 (35), p. 6131-6139.
10. Dosch, R. G. and Anthony, R. G. Topical Report: *"Hydrous Crystalline Silicotitanates: New Materials for Removal of Radiocesium from Concentrated Salt Solutions with pH's in the 1-14 Range"* Sandia National Laboratories, Albuquerque, NM, January 3, 1995.
11. Gu, D. PhD Thesis, *"TAM-5 A Hydrous Crystalline Silicotitanate for Removal of Cesium from Dilute Aqueous Waste"* Texas A & M University, 1995.

6.0 Acknowledgements

Bill Wilmarth and Fernando Fondeur (SRTC) for samples.

Paul Taylor (ORNL) for samples.

Jim Krumhansl and PengChu Zhang (SNL) for assistance with the DCP spectrometer.

APPENDIX A

Sample Log of Simulant-Treated IE-911 from ORNL and SRS

Table A-1 ORNL Temperature-Simulant Batch Studies

SNL sample name	Sample name/description	Cs K _α	XRD	SEM/EDS	TEM
mn6-1c	98-5 in Avg. Supernate simulant 12 mo/23 °C	860	Unaltered Na-CST	Colloidal precipitate of Na aluminosilicate on surface; phase 1, core-rim morphology increased	
mn6-1d	98-5 in Avg. Supernate simulant 86 day/50 °C 9 mo/23 °C	692	Phase 1* and Phase 3*** observable	Rims begin peeling off; outer layer has variable composition: either 1) CST-rich or 2) aluminosilicate (phase 1)	
mn6-1e	98-5 in Avg. Supernate simulant 86 day/80 °C 9 mo/23 °C	644	Phase 1 and Phase 3 continue forming	Core-rim morphology advanced, irregular-shaped spheres, flaked material	
mn6-1f	98-5 in Avg. Supernate simulant 86 day/120 °C 9 mo/23 °C	47	Predominantly Phase 1 Phase 2** And phase 3 degraded Na-CST	Engineered spheres broken and overgrown by types of crystals: Phase 3 20x100 μm Phase 1 mm size	Confirmed composition of phase 1 to be predominantly Na and S Confirmed composition of phase 3 to be predominantly Na and PM1
mn6-1g	98-5 in Avg. Supernate simulant 5 mo/23 °C	1100	Unaltered Na-CST		
mn6-1h	98-5 in Avg. Supernate simulant 5 mo/80 °C	740	Phase 1, possibly Phase 2 forming	Core-rim morphology, flakes, irregular shapes	

*Phase 1 is $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

**Phase 2 is $\text{Na}_3(\text{SO}_4)\text{X}$ (X=F, Cl)

***Phase 3 is $\text{Na}_7(\text{H}_3\text{O})(\text{PM1}_6\text{O}_{19})(\text{H}_2\text{O})_{14}$

Table A-2 SRS Simulant Composition Batch Studies

SNL sample name	Sample description*	XRD	SEM/EDS	Infrared Spectroscopy**
FF-CO₃	IE-911 in carbonate-containing avg. salt simulant	Na-form CST	Cemented and cracked pellets with Na aluminosilicate precipitation	O-H stretch at 1550 wavenumbers broadened And split
FF-C₂O₄	IE-911 in oxalate-containing avg. salt simulant	Na-form CST	Cemented and cracked pellets with Na aluminosilicate precipitation	O-H stretch at 1550 wavenumbers broadened And split
FF-NO₃-pt-c	Pretreated IE-911 in high nitrate simulant solution	Na-form CST	Cemented and cracked pellets with Na aluminosilicate precipitation	
FF-NO₃-ar-c	As Received IE-911 in high nitrate simulant solution	Na-form CST	Cemented and cracked pellets with Na aluminosilicate precipitation	
FF-OH-pt-c	Pretreated IE-911 in high hydroxide simulant solution	Na-form CST	Cemented and cracked pellets with Na aluminosilicate precipitation	
FF-OH-ar-c	As received IE-911 in high hydroxide simulant solution	Na-form CST Na ₈ (Al ₆ Si ₆ O ₂₄)(N O ₃) ₂ •4H ₂ O	Cemented and cracked pellets with Na aluminosilicate precipitation	
FF-ave-pt-c With H₂O₂	Pretreated IE-911 in avg. simulant solution with H ₂ O ₂	Na-form CST, broad low angle peak at 9.4 Å	Cemented and cracked pellets with Na aluminosilicate precipitation	O-H stretch at 1550 wavenumbers broadened And split
FF-ave-ar-c	As received IE-911 in average salt solution	Na-form CST plus Na ₈ (Al ₆ Si ₆ O ₂₄)(N O ₃) ₂ •4H ₂ O	Cemented and cracked pellets with Na aluminosilicate precipitation	
FF-DI H₂O-pt-c	Pretreated IE-911 in DI H ₂ O	Na-form CST	Cemented and cracked pellets	O-H stretch at 1550 wavenumbers broadened
FF-DI H₂O-ar-c	As received IE-911 in DI H ₂ O	Acidified CST	Smooth, featureless engineered spheres	As received

*All samples are batch 99-9, soaked in different solutions for 2 months at room temperature.

**IR studies done on this suite of samples to determine if anions/ligands (H₂O₂ C₂O₄ CO₃) adsorb onto CST surface or pores

Table A-3 ORNL Column Studies

SNL sample name	Sample description*	Cs K _α	XRD	SEM/EDS
mn6-1i	98-5 in Avg. Supernate simulant from column recirculating for 4.5 mo	1100	Phase 1, possibly Phase 3 forming	Very advanced core-rim morphology with thick rims: 50-100 microns with mixed composition: CST, binder, aluminosilicate
mn6-1j	98-5 in high pH salt supernate simulant from column recirculating for 4.5 mo	1200	Unaltered Na-CST	1-5 mo: column, avg. salt sln (1.9 M NaOH) these samples have increasing rim/core development with increasing aluminosilicate (phase 1) surface alteration.
mn6-3a	98-5 in avg. simulant salt from mid-column 1 month (C-AVG-M-1M)	1214	Unaltered Na-CST	
mn6-3b	98-5 in avg. simulant salt from mid-column 2 month (C-AVG-M-2M)	1487	Unaltered Na-CST	
mn6-3c	98-5 in avg. simulant salt from mid-column 3 month (C-AVG-M-3M)	1084	Unaltered Na-CST	
mn6-3d	98-5 in avg. simulant salt from mid-column 4 month (C-AVG-M-4M)	1047	Unaltered Na-CST	'Freshly exposed' surfaces of the core have relatively little sodium aluminosilicate coating
mn6-3e	98-5 in avg. simulant salt from mid-column 5 month (C-AVG-M-5M)	1037	Na-CST plus minimal phase 1	
mn6-4a	98-5 in high salt simulant from mid-column 1 month (C-HS-M-1M)	1220	Unaltered Na-CST	This series of samples has negligible Na aluminosilicate deposits on the surface. However, they do exhibit the core/rim development. This suggests the Na aluminosilicate deposits and core-rim morphology are not necessarily related
mn6-4b	98-5 in high salt simulant from mid-column 2 month (C-HS-M-2M)	1565	Unaltered Na-CST	
mn6-4c	98-5 in high salt simulant from mid-column 3 month (C-HS-M-3M)	1221	Unaltered Na-CST	
mn6-4d	98-5 in high salt simulant from mid-column 4 month (C-HS-M-4M)	1204	Unaltered Na-CST	
mn6-4e	98-5 in high salt simulant from mid-column 5 month (C-HS-M-5M)	1279	Unaltered Na-CST	

*Phase 1 is $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

***Phase 3 is $\text{Na}_7(\text{H}_3\text{O})(\text{Nb}_6\text{O}_{19})(\text{H}_2\text{O})_{14}$

APPENDIX B

Additional XRPD Spectra of IE-911 Samples from ORNL and SRS

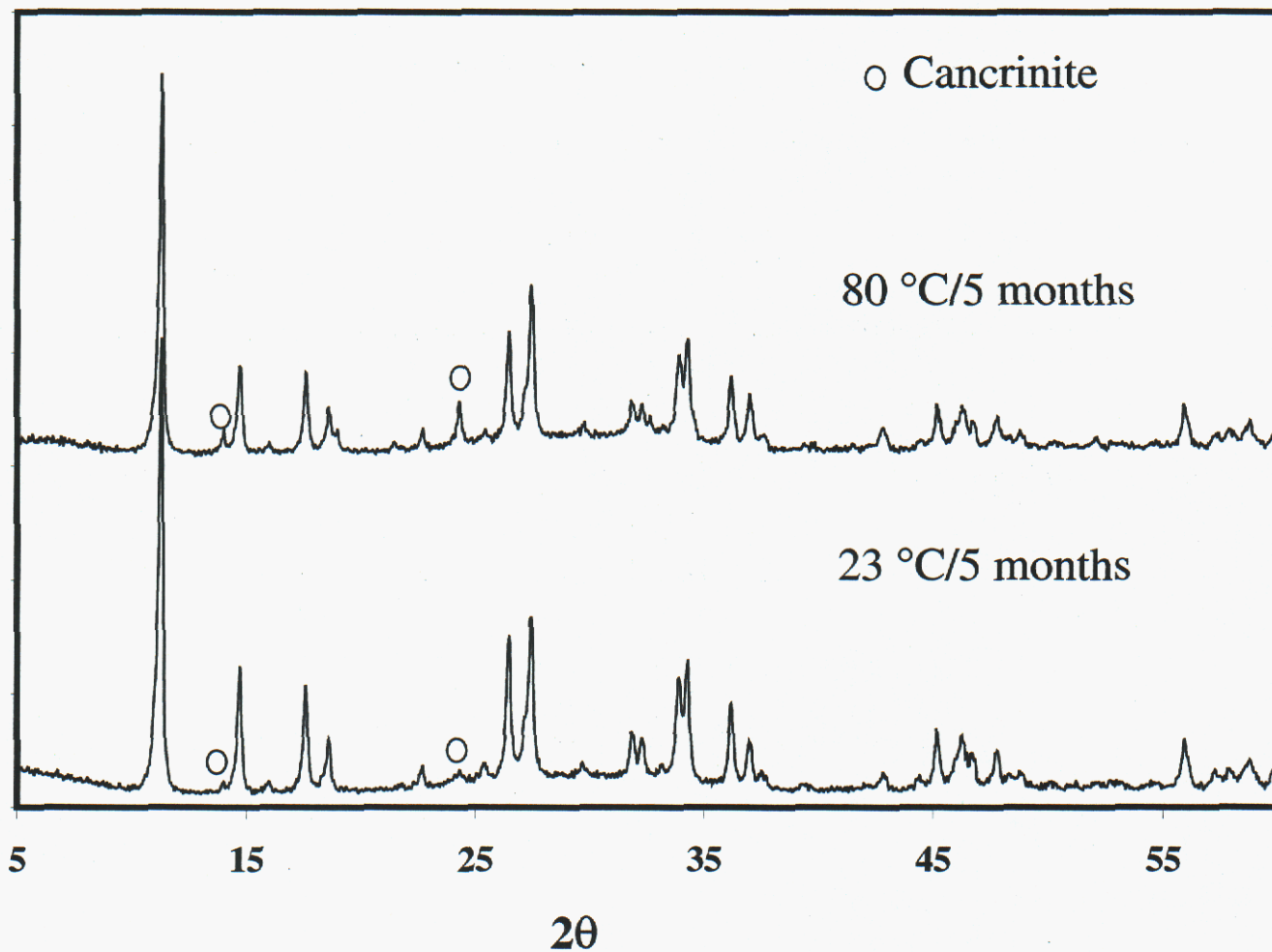


Figure B-1. XRPD spectra of batch treatment of IE-911 in average simulant at 23 °C and 80 °C for 5 months each, showing some cancrinite formation (ORNL study).

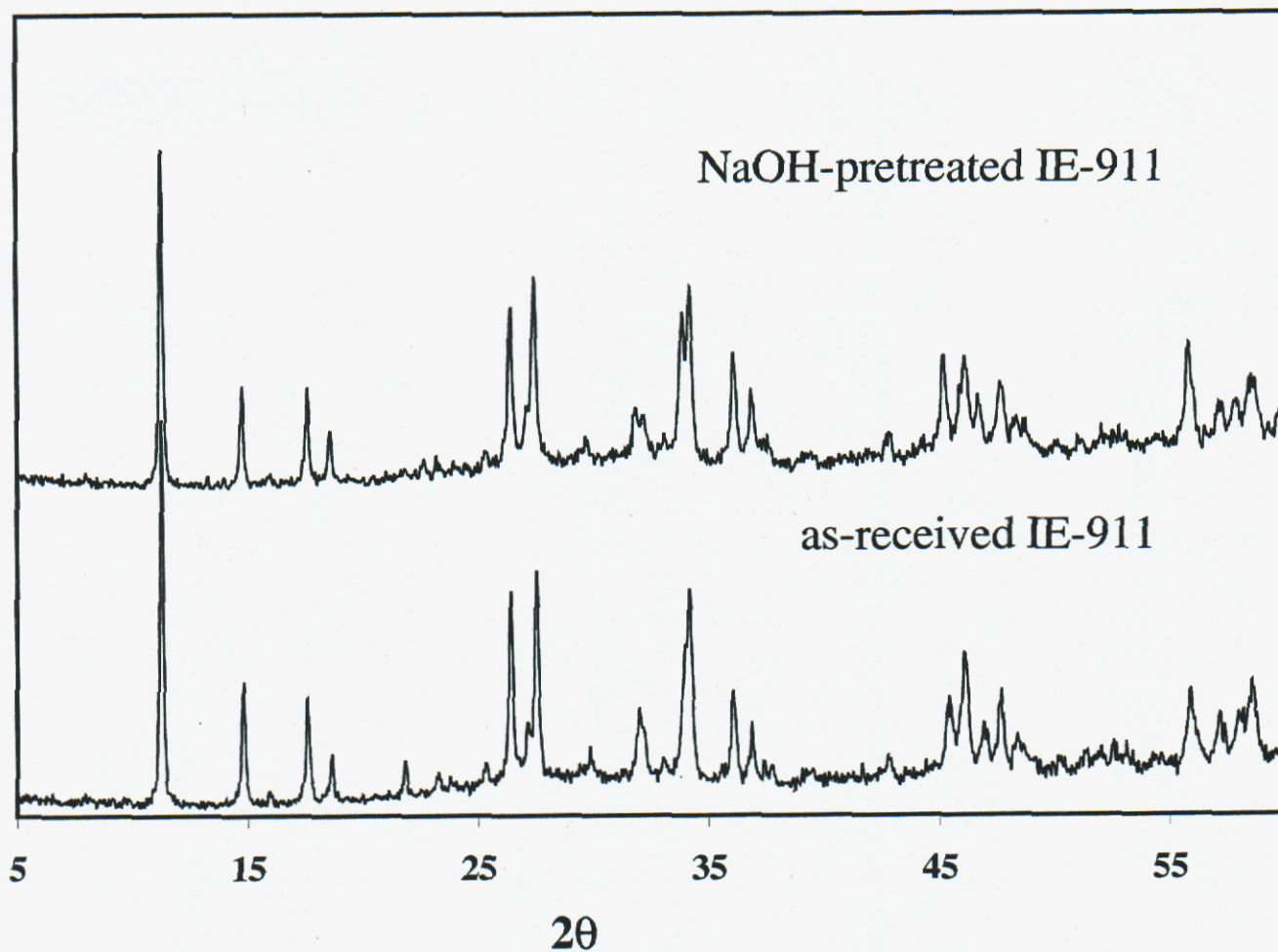


Figure B-2. XRPD spectra of IE-911, as-received and NaOH-pretreated; exposed to deionized water for 2 months each at room temperature (SRS study).

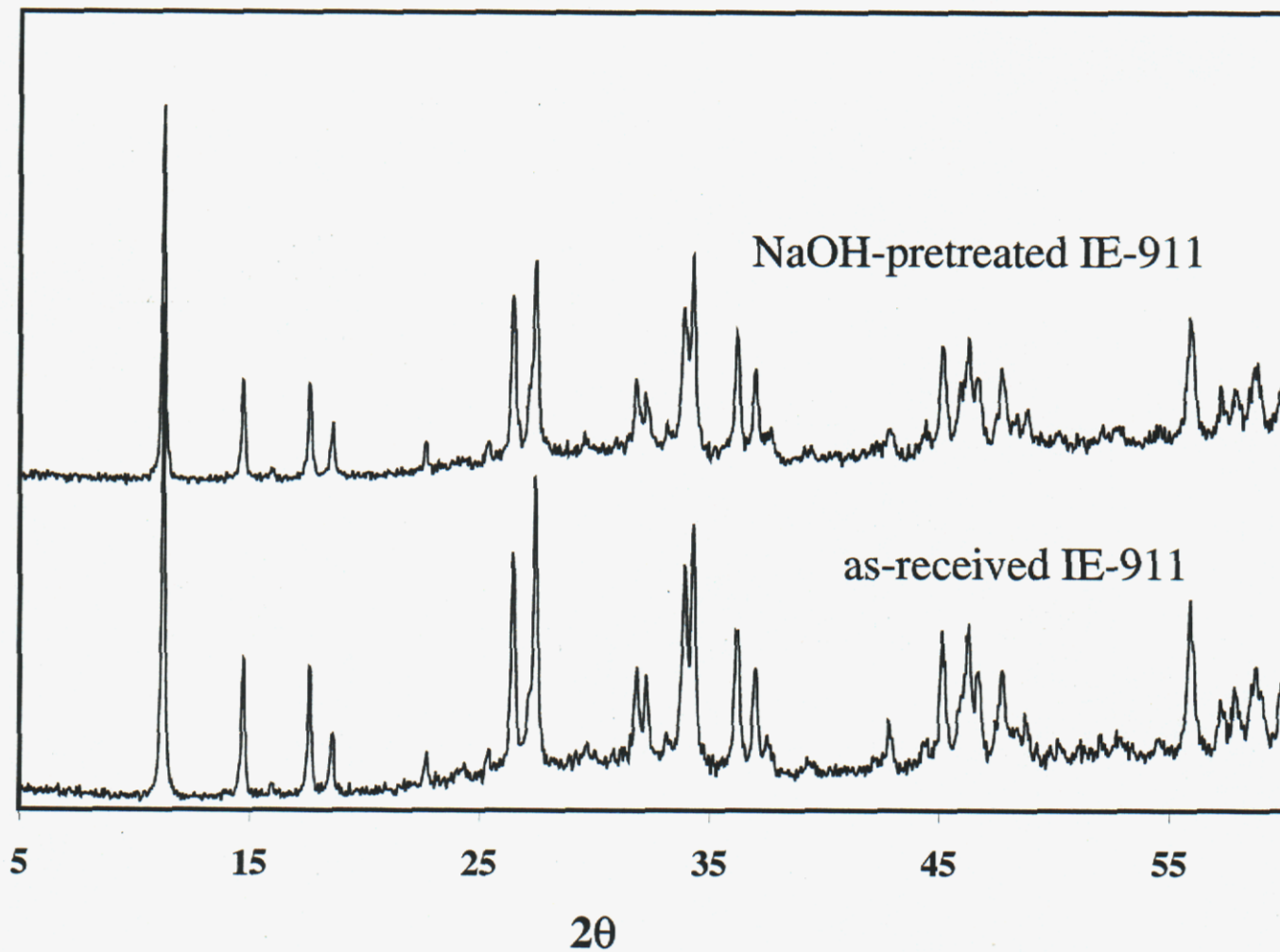


Figure B-3. XRPD spectra of IE-911, as-received and NaOH-pretreated; exposed to high nitrate simulant solution for 2 months each at room temperature (SRS study).

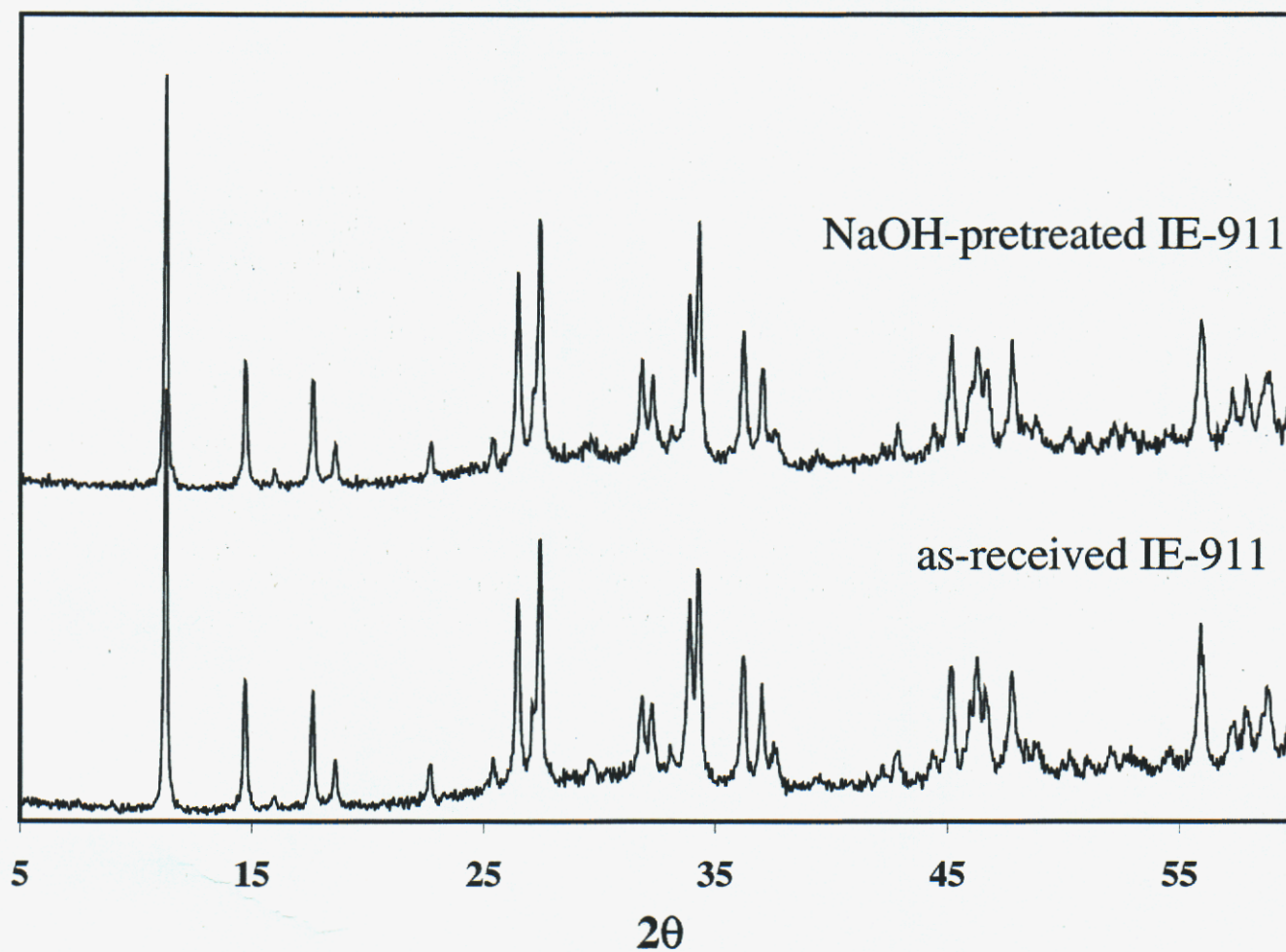


Figure B-4. XRPD spectra of IE-911, as-received and NaOH-pretreated; exposed to high hydroxide simulant solution for 2 months each at room temperature (SRS study).

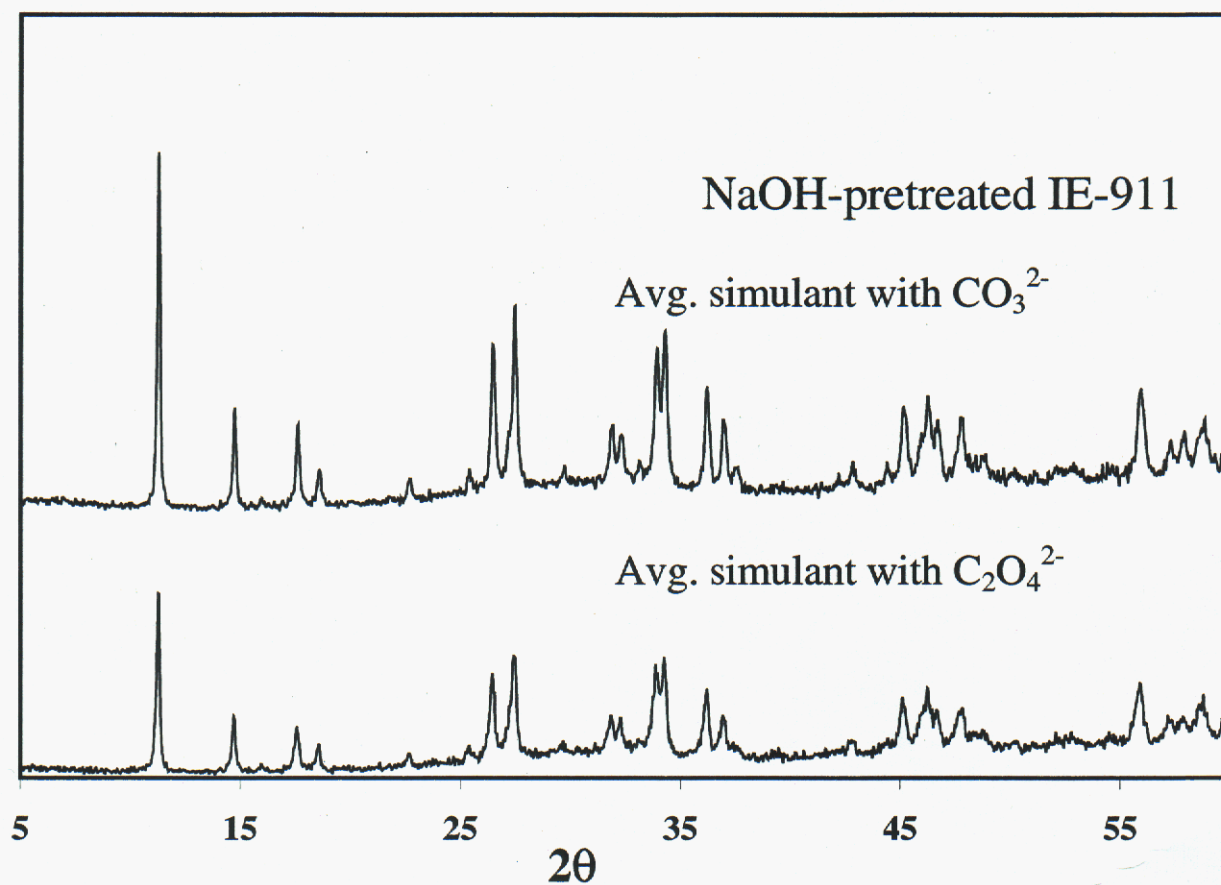


Figure B-5. XRPD spectra of IE-911 exposed to average simulant solution containing $\text{C}_2\text{O}_4^{2-}$ (bottom) and CO_3^{2-} (top) for 2 months each at room temperature (SRS study).

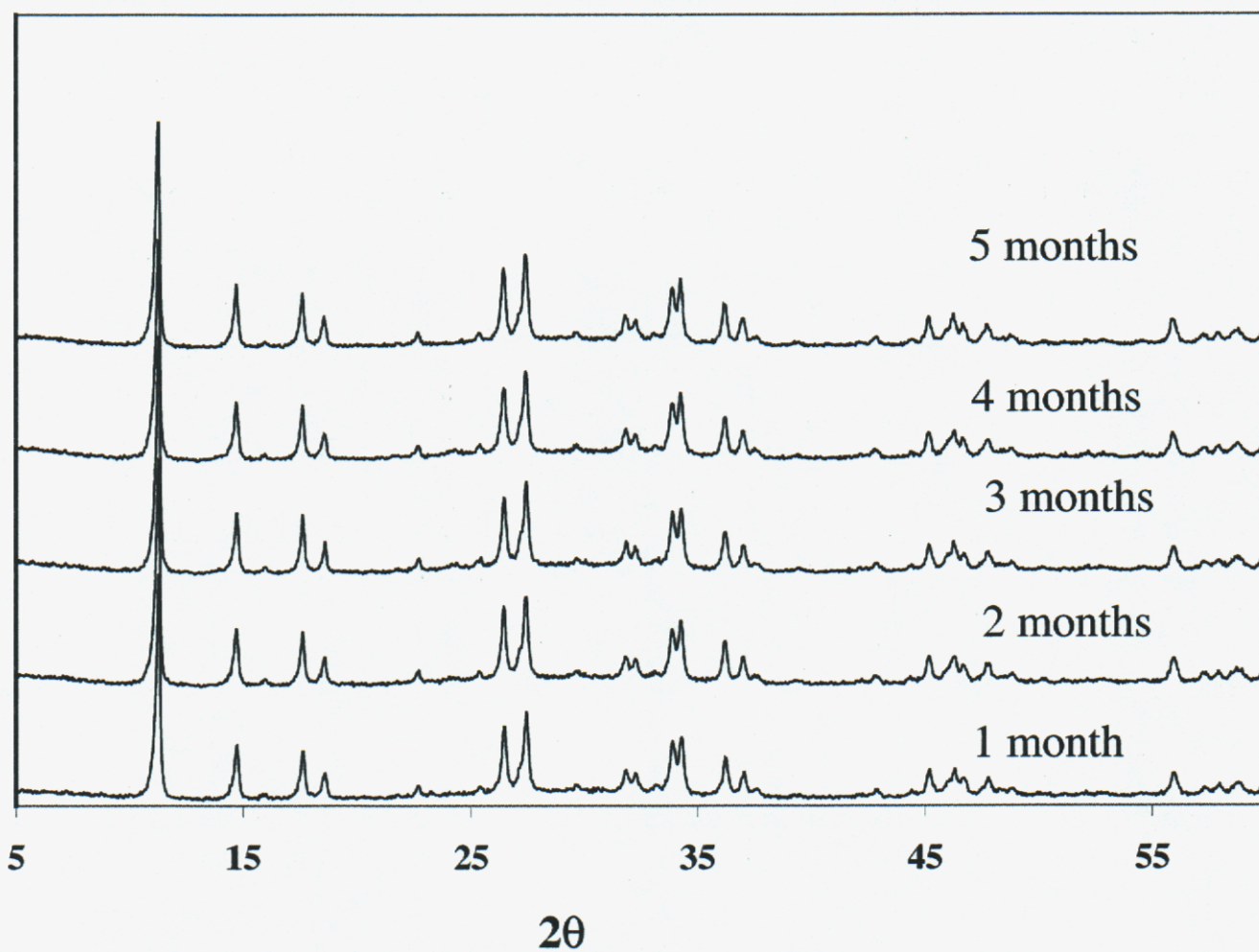


Figure B-6. IE-911 in a recirculating column of high pH salt solution at room temperature for 1-5 months.

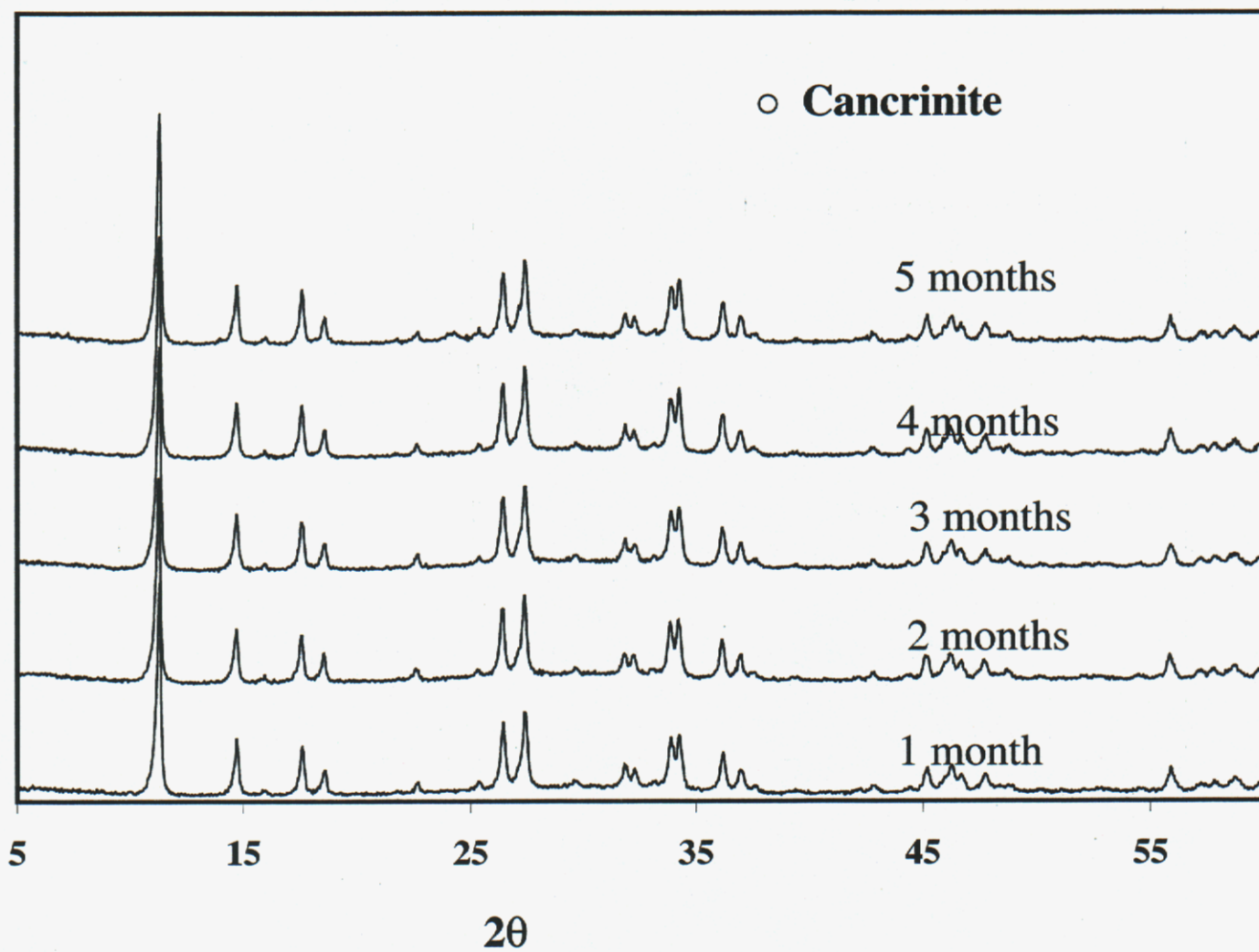


Figure B-7. IE-911 in a recirculating column of average salt solution at room temperature for 1-5 months.

APPENDIX C

Addendum on Exfoliation and Cracking Phenomenon

Since the initial release of this information in the form of a report to DOE personnel on October 27, 2000, **the direct cause of the cracking/exfoliation of simulant-exposed or NaOH-pretreated IE-911 has been revealed** through continued investigation. The purpose of this appendix is to update the information contained in this report regarding this cracking/exfoliation observed by SEM. Since this phenomenon was observed consistently only at Sandia National Laboratories (and not at any of the other participating laboratories), we investigated our instrumentation and sample preparation techniques. Sample preparation for SEM involves carbon-coating the sample to eliminate the effect of charging. The first step of carbon-coating is degassing the carbon filament in a vacuum chamber. During degassing, the filament heats up, and also heats the sample inside the vacuum chamber. It is this combination of heat and vacuum that causes the cracking and exfoliation of some simulant- and NaOH-treated IE-911 pellets. Follow-up experiments revealed that heat only or vacuum only does not result in the same cracking/exfoliation. The combination of both heat and vacuum is necessary.

Although the direct cause of cracking/exfoliation of IE-911 is a technique which is irrelevant to waste treatment applications; there is still some concern that cracking/exfoliation occurs only in IE-911 which has been previously exposed to simulant or sodium hydroxide. This suggests NaOH- or simulant-treatment causes the IE-911 surface to become somewhat brittle. Binder behavior upon exposure to NaOH solutions has been investigated (see SAND-2001-0999), to determine if the surface becomes brittle by binder condensation and cross-polymerization reactions.

DISTRIBUTION LIST:

Sandia National Laboratories Personnel

Organization 6118, Mailstop 0750
Jim Krumhansl
Organization 6233, Mailstop 0755
May Nyman (5)
Organization 6233, Mailstop 0755
Tina Nenoff
Organization 6233, Mailstop 0755
D. S. Horschel
Organization 1822, Mailstop 1411
T. J. Headley
Organization 6803, Mailstop 0734
Larry Bustard
Organization 6118, Mailstop 0750
Hank Westrich
Organization 6233, Mailstop 0750
Department File
Technical Library: Organization 9616, Mailstop 0899 (2)
Central Technical Files: Organization 8945-1, Mailstop 9018
Review and Approval Desk: Organization 9612, Mailstop 0612
For DOE/OSTI

Non-Sandia National Laboratories Personnel

Yali Su
Battelle
Pacific Northwest National Lab
P.O. Box 999 / MS K8-93
Richland, WA 99352
Liyu Li
Battelle
Pacific Northwest National Lab
P.O. Box 999 / MS K8-93
Richland, WA 99352
Jim Buelt
Battelle
Pacific Northwest National Lab
P.O. Box 999 / MS K9-09
Richland, WA 99352
Dennis Wester
Battelle
Pacific Northwest National Lab
P.O. Box 999 / MS P7-25

Richland, WA 99352

Steve Schlahta, PNNL

C/o Westinghouse Savannah River Company

Building: 704-3N (Room: N302)

Aiken, SC 29808

Harry Harmon

C/o Westinghouse Savannah River Company

Building 704-3N (Room N111)

Aiken, SC 29808

Paul Taylor

Oak Ridge National Laboratory

1 Bethel Road (Building 4501)

Oak Ridge, TN 37831

Tim Kent

Oak Ridge National Laboratory

1 Bethel Road (Building 4501)

Oak Ridge, TN 37831

Bill Wilmarth

Savannah River Technology Corp.

Building: 773-42A (Room: 153)

Aiken, SC 29808

Doug Walker

Savannah River Technology Corp.

Building: 773-A (Room: B-124)

Aiken, SC 29808

Fernando Fondeur

Savannah River Technology Corp.

Building: 773-A (Room: B-124)

Aiken, SC 29808

Sam Fink

Savannah River Technology Corp.

Building: 773-A (Room: B-112)

Aiken, SC 29808

Roy Jacobs

Westinghouse Savannah River Corp.

Building: 704-3N (Room: S311)

Aiken, SC 29808

Jeff Pike

Westinghouse Savannah River Corp.
Building: 704-196N (Room: N401)
Aiken, SC 29808

Joe Carter

Westinghouse Savannah River Corp.
Building: 704-3N (Room: S151)
Aiken, SC 29808

Jim McCullough

U.S. Department of Energy, Savannah River
Building: 704-3N (Room: N380)
Aiken, SC 29808

Patricia Suggs

U.S. Department of Energy, Savannah River
Building: 704-3N (Room: 380A)
Aiken, SC 29808

John Reynolds

U.S. Department of Energy, Savannah River
Building: 704-3N (Room: N152)
Aiken, SC 29808

Rich Braun

UOP
25 East Algonquin Rd
Des Plaines, IL, 60017

Nan Greenlay

UOP
25 East Algonquin Rd
Des Plaines, IL, 60017

Dennis Fennelly

UOP Molecular Sieves, Suite 207
307 Fellowship Road
Mt. Laurel, N.J. 08054